JOURNAL
OF
THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS
ON
ORGANIC, PHYSIOLOGICAL, AND AGRICULTURAL CHEMISTRY.

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JOURNALS FROM WHICH ABSTRACTS ARE MADE.

All references to Journals should give the abbreviated title, the year of publication, the series, the volume and the page; thus *Ber.* 1901, **34**, 2455; *Bull. Soc. chim.* 1901, [iii], **25**, 794; *Gazzetta* 1901, **31**, i, 554.

Abbreviated Title.	Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Bot.	Annals of Botany.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Applicata.	Annali di Chimica Applicata.
Ann. Chim.	Annales de Chimie
Ann. Falsif.	Annales des Falsifications.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. Physik	Annalen der Physik.
Ann. Physique	Annales de Physique.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Ann. Soc. Quím. Argentina.	Annales de la Sociedad Química Argentina.
Arch. expt. Path. Pharm.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Hygiene	Archiv für Hygiene.
Arch. Néerland.	Archives Néerlandaises des sciences exactes et naturelles.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arkiv Kem. Min. Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Atti R. Accad. Sci. Torino.	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Ber. Deut. physikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
* *Bied. Zentr.*	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Biochem. Bull.	Biochemical Bulletin.
Biochem. J.	The Biochemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Boll. chim. farm.	Bollettino chimico farmaceutico.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Acad. Sci. Roumaine	Bulletin de la Section Scientique de l'Académie Roumaine.
Bull. Acad. Sci., Petrograd.	Bulletin de l'Académie Impériale des Sciences de St. Pétersbourg.
Bull. Assoc. chim. Sucr. Dist.	Bulletin de l'Association des chimistes de Sucrerie et de Distillerie.
Bull. Geol. Soc. Amer.	Bulletin of the Geological Society of America.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. ind. Mulhouse	Bulletin de la Société industrielle de Mulhouse.
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Palaeontologie.
* *Chem. Zentr.*	Chemisches Zentralblatt.

* Abstracts from the *Zentralblatt* are made only in the case of papers published in journals other than those included in this list.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

Abbreviated Title.	Journal.
Chem. News	Chemical News.
Chem. Rev. Fett-Harz-Ind.	Chemische Revue über die Fett- und Harz-Industrie.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Exper. Stat. Record	Experiment Station Record.
Gazzetta	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Int. Zeitsch. phys.-chem. Biol.	Internationale Zeitschrift für physikalisch-chemische Biologie.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band.
Jahrb. Radioaktiv. Elektronik	Jahrbuch der Radioaktivität und Elektronik.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Biol. Chem.	Journal of Biological Chemistry, New York.
J. Chim. phys.	Journal de Chimie physique.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Geol.	Journal of Geology.
J. Hygiene	Journal of Hygiene.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Landw.	Journal für Landwirtschaft.
J. Med. Research	Journal of Medical Research.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Roy. Soc. New South Wales.	Journal of the Royal Society of New South Wales.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers	Journal of the Society of Dyers and Colourists.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
K. Svenska Vet-Akad. Handl.	Kongl. Svenska Vetenskaps-Akademiens Handlingar.
Kolloid Zeitsch.	Kolloid Zeitschrift.
Koll. Chem. Beihefte	Kolloidchemische Beihefte.
Lancet.	The Lancet.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Le Radium	Le Radium.
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Coll. Sci. Eng. Kyōtō.	Memoirs of the College of Science and Engineering, Kyōtō Imperial University.
Mem. Dept. Agric. India	Memoirs of the Department of Agriculture in India.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Metallurgie	Metallurgie.
Milch. Zentr.	Milchwirtschaftliches Zentralblatt.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Nuovo Cim.	Il Nuovo Cimento.
Pflüger's Archiv.	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. J.	Pharmaceutical Journal.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zeit.	Pharmazeutische Zeitung.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

Abbreviated Title.	Journal.
Pharm. Zentr-h.	Pharmazeutische Zentralhalle.
Philippine J. Sci.	Philippine Journal of Science.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Proc. Amer. Physiol. Soc.	Proceedings of the American Physiological Society.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Phil. Soc. Glasgow	Proceedings of the Glasgow Philosophical Society.
Proc. Physical Soc. London	Proceedings of the Physical Society of London.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Quart. J. exp. Physiol.	Quarterly Journal of experimental Physiology.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rend. Accad. Sci. Fis. Mat. Napoli.	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche-Napoli.
Rev. de Métallurgie	Revue de Métallurgie.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Sitzungsber. K. Akad. München.	Sitzungsberichte der königlich bayerischen Akademie der Wissenschaften zu München.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Path. Soc.	Transactions of the Pathological Society.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans. Roy. Soc. Edin.	Transactions of the Royal Society of Edinburgh.
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
Tsch. Min. Mitt.	Tschermak's Mineralogische Mitteilungen.
U.S.A. Dept. Agric. Bull.	Bulletins of the Department of Agriculture, U.S.A.
U.S.A. Dept. Agric. Rep.	Reports of the Department of Agriculture, U.S.A.
Verh. Ges. deut. Naturforsch. Aerzte	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
Wiss. Abhandl. Phys.-Tech. Reichsanstalt.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Biol.	Zeitschrift für Biologie.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeitsch. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeitsch. prakt. Geol.	Zeitschrift für praktische Geologie.
Zeitsch. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Zeitsch. wiss. Photochem.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Zeitsch. Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen.

JOURNAL

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Preparation of Butadiene and its Homologues. W. H. PERKIN, jun., and F. E. MATTHEWS (Brit. Pat. 15049 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 806).—Butadiene and its homologues are obtained by subjecting olefines to the action of oxidising agents or of substances which combine with hydrogen at elevated temperatures, with or without the use of catalysts. C. S.

Preparation of Isoprene. HOOD RUBBER CO. (U.S. Pat. 1106290; from *J. Soc. Chem. Ind.*, 1914, **33**, 942).—The vapour of methyl *iso*propyl ketone is passed over a dehydrating catalyst, such as aluminium silicate, at 400—600° under reduced pressure, and the isoprene is separated from the other products. C. S.

Preparation of Trichloroethylene from *s*-Tetrachloroethane. CHEMISCHE FABRIK BUCKAU (D.R.-P. 274782; from *J. Soc. Chem. Ind.*, 1914, **33**, 807).—*s*-Tetrachloroethane may be converted into trichloroethylene, without formation of hexachlorobenzene, by passing its vapour over a catalyst in presence of thorium oxide at a temperature not exceeding 390°. T. H. P.

Preparation of Orthovanadic Esters and their Solutions L. HESS (D.R.-P. 273220; from *J. Soc. Chem. Ind.*, 1914, **33**, 712).—Vanadium pentoxide dissolves in primary, secondary or tertiary mono- or polyhydric alcohols, with formation of esters of the type R_3VO_4. *Ethyl vanadate*, Et_3VO_4, is a faintly yellow liquid, b. p. 108°/26 mm.,

D^{15} 1·167, the iso*propyl* ester a yellow liquid, b. p. 124°/21 mm., and the *amyl* ester a liquid, b. p. 161°/19 mm., D^{15} 0·993. T. H. P.

Preparation of Esters of Tertiary Alcohols. NEUMANN & Co. and J. ZELTNER (Fr. Pat. 466804; from *J. Soc. Chem. Ind.*, 1914, **33**, 845).—Tertiary alcohols are esterified by treating them with acid chlorides in the presence of tertiary bases, such as pyridine or dimethylaniline. In some cases the reaction is facilitated by gentle heating. C. S.

Preparation of Esters and Ethers of Ethylidene Glycol and of Vinyl Alcohol. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (U.S. Pat. 1084581; Brit. Pat. 14246 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 219).—Acetylene reacts with various organic hydroxy-compounds in the presence of a mercury salt (mercuric sulphate) to form ethers and esters of ethylidene glycol and of vinyl alcohol. C. S.

Preparation of Carbamic Esters of α-Dichlorohydrin. B. BECKMANN and BRUNO BECKMANN (Brit. Pat. 25971 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 439).—The *carbamic* ester of α-dichlorohydrin is obtained by the action of carbamyl chloride on α-dichlorohydrin. It crystallises in colourless needles, m. p. 82—83°, and has pronounced narcotic properties. C. S.

Preparation of Acetic Acid from Acetylene. FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (Fr. Pat. 467515; from *J. Soc. Chem. Ind.*, 1914, **33**, 830).—Acetylene is converted into acetic acid by passing it through a solution of hydrogen peroxide, persulphuric acid, monopersulphuric acid, or a salt of one of these acids, in the presence of mercury or a mercury compound. For example, acetylene (10·8 parts by weight) is passed into a mixture of 250 parts of 20—30% sulphuric acid, 100 parts of 95% ammonium persulphate, and 5—10 parts of mercuric oxide at 30—40°. The resulting liquid contains 24—25 parts of acetic acid. C. S.

Electrolytic Method of Converting Acetylene into Acetic Acid. FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (Fr. Pat. 467778; from *J. Soc. Chem. Ind.*, 1914, **33**, 830).—The anodic oxidation of acetylene to acetic acid can be effected in a satisfactory manner by using a solution of sulphuric acid or other acid solution as electrolyte, in the presence of a mercury compound. For example, the anodic compartment of an electrolytic cell, provided with a clay diaphragm and a lead anode, is filled with 30% sulphuric acid containing 1—2% of mercuric oxide; the cathode, made of lead or copper, is also immersed in 30% sulphuric acid. Acetylene is passed into the anodic compartment at the rate of 48·5 grams per hour per 100 amperes. The voltage is 3—4·5 volts, the current density at the anode is 5—15 amperes/dcm.^{2}, and the temperature of the electrolyte is 30—40°. The yield of acetic acid is 0·5 kilo. or more per litre of anolyte in twenty-four hours. C. S.

Preparation of Acetic Acid from Acetaldehyde. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (Fr. Pat. 460971; from *J. Soc. Chem. Ind.*, 1914, **33**, 42).—The conversion of acetaldehyde into acetic acid by oxygen is accelerated by the addition of small quantities of manganese compounds; the reaction is not explosive, as is the case when compounds of chromium, vanadium, cerium, etc., are used as accelerators. For example, a current of dry oxygen is passed into a mixture of 300 kilo. of pure acetaldehyde and 2 kilo. of manganese acetate in a pure aluminium vessel provided with a stirrer and a cooling jacket. The manganese salt dissolves in the aldehyde, and the solution absorbs oxygen very energetically, the heat developed being removed by external cooling. The absorption is complete after ten to twenty hours, and the acid is distilled.

Air may be used in place of oxygen, and the gases may be introduced under pressure; acetic acid or other solvent may be added to the aldehyde, if desired. C. S.

Preparation of Ethyl Acetate from Acetaldehyde. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (Brit. Pat. 26825 and 26826 of 1913; Fr. Pat. 465965; from *J. Soc. Chem. Ind.*, 1914, **33**, 666—667).—I. Acetaldehyde is converted almost quantitatively into ethyl acetate by means of small amounts of aluminium alkyloxides in the presence of catalysts, particularly haloids such as those of tin, aluminium, or silicon, which are by themselves incapable of forming ethyl acetate from acetaldehyde. For example, six parts of aluminium ethoxide containing about 10% of aluminium chloride are gradually added to 135 parts of acetaldehyde; after keeping for ten hours, ethyl acetate (123 parts) is removed by distillation.

II. Instead of using an aluminium alkyloxide and another catalyst, the product obtained by treating an aluminium alkyloxide with water, or a substance containing water, may be employed to convert acetaldehyde into ethyl acetate. The most active of the products of this class appear to be those containing 16—25% of aluminium. C. S.

Preparation of Acetic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (Brit. Pat. 10377 of 1914; from *J. Soc. Chem. Ind.*, 1914, **33**, 961).—Acetaldehyde, mixed with about 1% of its weight of a catalyst, especially ceric oxide, is treated with oxygen under a pressure of about 2 atmos., or with air at a somewhat higher pressure, for five hours, cooling being resorted to after the temperature has risen spontaneously to 50—60°. The yield of acetic acid is 95% of the theoretical. C. S.

Preparation of Anhydrides of Organic Acids, or of Mixtures of the Anhydrides and the Acids. R. MULLER and DEUTSCHE CELLULOID FABRIK (Fr. Pat. 468963; from *J. Soc. Chem. Ind.*, 1914, **33**, 985).—Acetic anhydride is produced almost quantitatively by passing the vapours of nitrogen pentoxide or a mixture of the oxides of nitrogen and air or oxygen over sodium or calcium acetate. When the materials are not dry, mixtures of acetic anhydride and acetic acid are produced.

The anhydride, or mixture of anhydride and acid, may be separated from the nitrate by extraction or by heating in a vacuum. The product contains only traces of oxides of nitrogen, which are easily removed by distillation over acetates.

The reaction can be carried out equally well by passing oxides of nitrogen into indifferent liquids containing the metallic acetate in solution or suspension. The same process is applicable to the production of other organic anhydrides. C. S.

Some Salts of the Chloroacetic Acids. W. G. BATEMAN and A. B. HOEL (*J. Amer. Chem. Soc.*, 1914, **36**, 2517—2521).—As comparatively little has been recorded with reference to the derivatives of the chloroacetic acids, a study of some of their salts has been carried out. The following salts are described.

Ammonium chloroacetate, $CH_2Cl\cdot CO_2NH_4$, white crystals, stable, and not deliquescent; ammonium trichloroacetate, $CCl_3\cdot CO_2NH_4$; *copper chloroacetate*, $(CH_2Cl\cdot CO_2)_2Cu,4H_2O$, deep green crystals, and the anhydrous salt, obtained as a bluish-green powder; *zinc chloroacetate*, $(CH_2Cl\cdot CO_2)_2Zn,2H_2O$, deliquescent, transparent crystals; *lead chloroacetate*, $(CH_2Cl\cdot CO_2)_2Pb$, white, prismatic plates; *manganese chloroacetates*, $(CH_2Cl\cdot CO_2)_2Mn,CH_2Cl\cdot CO_2H,4H_2O$ and $(CH_2Cl\cdot CO_2)_2Mn,CH_2Cl\cdot CO_2H,2H_2O$, white crystals; *nickel chloroacetate*, $(CH_2Cl\cdot CO_2)_2Ni,3H_2O$, apple-green crystals; *phenylhydrazine chloroacetate*, $NHPh\cdot NH_2,2CH_2Cl\cdot CO_2H$, white needles; *carbamide chloroacetate*, $CO(NH_2)_2,CH_2Cl\cdot CO_2H,EtOH$, large, leafy crystals. Aniline and *p*-toluidine also yield crystalline chloroacetates. Basic chloroacetates of iron and chromium were obtained. E. G.

Preparation of Acylsulphuric Acids and of their Salts with Alkali or Alkaline Earth Metals. NAAMLOOZE VENNOOTSCHAP FABRIEK VAN CHEMISCHE PRODUCTEN (Fr. Pat. 461539; from *J. Soc. Chem. Ind.*, 1914, **33**, 219).—The conversion of monocarboxylic acids or their anhydrides into sulphonic acids by the action of sulphur trioxide or fuming sulphuric acid is found to take place in two stages, the first step being the formation of an acylsulphuric acid, for example, $CH_3\cdot CO\cdot O\cdot SO_3H$, which is rapidly converted into the sulphonic acid (sulphoacetic acid) at the ordinary temperature. The second step is very slow, however, at temperatures below 0°, so that the acylsulphuric acids can be prepared by carrying out the reaction at low temperatures. For example, a quantitative yield of acetylsulphuric acid is obtained by adding gradually 80 kilo. of sulphur trioxide to 60 kilo. of acetic acid at a temperature below 0°. The acylsulphuric acids thus formed are converted into the alkali or alkaline earth salts by mixing them with a suitable, anhydrous salt of the alkali or alkaline earth metals below 0°. C. S.

Preparation of Anhydrides of Monobasic Carboxylic Acids. NAAMLOOZE VENNOOTSCHAP FABRIEK VAN CHEMISCHE PRODUCTEN (Fr. Pat. 461540; Brit. Pat. 12402 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 219).—The alkali or alkaline-earth salts of acylsulphuric

acids (preceding abstract) are converted into the corresponding carboxylic anhydrides by heating, alone or in the presence of an indifferent liquid, such as acetic acid. Simple or mixed anhydrides are also obtained by heating alkali or alkaline-earth acylsulphates with alkali or alkaline-earth salts of monocarboxylic acids. The preparation of acetic anhydride from sodium sulphoacetate and sodium acetate is described in detail. C. S.

Alcoholysis of Esters. ANTONIO MADINAVEITIA (*Anal. Fis. Quim.*, 1914, **12**, 426—428).—When esters are boiled with methyl or ethyl alcohol in presence of hydrochloric acid, the alcohol residue is displaced by methyl or ethyl, the corresponding alcohol being liberated. The method has been applied to castor oil, almond oil, butter, spermaceti, *iso*amyl acetate, *cyclo*hexyl acetate, and phenyl acetate. A. J. W.

Cryoscopic Studies of Organic Complexes of Permolybdic Acid. II. A. MAZZUCCHELLI and C. RANUCCI (*Gazzetta*, 1914, **44**, ii, 426—437. Compare A., 1914, i, 1124).—The authors have determined the freezing points of mixtures of molybdic acid with hydrogen peroxide, and have also carried out cryoscopic and conductivity measurements on mixtures of ozomolybdic acid with various organic acids. The results show that malic acid forms with ozomolybdic acid the complexes $C_4H_6O_5,MoO_4$ and $2C_4H_6O_5,MoO_4$, but they give no indication of the existence of a complex, $C_4H_6O_5,2MoO_4$, analogous to the derivative of molybdic acid, $C_4H_6O_5,2MoO_3$. The action of hydrogen peroxide on the sodium salt of the latter acid appears to yield an unstable additive product, which undergoes rapid hydrolysis with formation of colloidal ozomolybdic acid. Quinic acid and ozomolybdic acid give rise to the complex, $2C_7H_{12}O_6,MoO_4$; cryoscopic and electrolytic determinations of the dissociation constant of this complex yield somewhat divergent values, just as was found to be the case with molybdoquinic acid, $2C_7H_{12}O_6,MoO_3$ (*loc. cit.*). T. H. P.

Resolution of Ascaridolic Acid. E. K. NELSON (*J. Amer. Chem. Soc.*, 1914, **36**, 2521—2522).—Ascaridolic acid, which has the structure of αδ-cineolic acid (A., 1913, *i*, 190), has been resolved by the fractional crystallisation of its cinchonidine salt into *d*-ascaridolic acid, $[\alpha]_D + 13{\cdot}93°$, m. p. 129—130°, and *l*-ascaridolic acid, $[\alpha]_D - 13{\cdot}77°$, m. p. 129—130°. E. G.

Preparation of Acetaldehyde from Acetylene. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (Fr. Pat. 460553; U.S. Pat. 1107019; from *J. Soc. Chem. Ind.*, 1914, **33**, 42).—The conversion of acetylene into acetaldehyde by means of solutions of mercury salts is retarded, after the reaction has proceeded for some time, by the accumulation of the vapour of the aldehyde in the gaseous mixture above the solution. The process can be carried out rapidly, continuously, and without retardation, by passing an excess of acetylene through solutions of mercury salts, extracting the aldehyde from the gas immediately, and again passing the acetylene through the solution. The process described in Fr. Pat. 455370 is considerably accelerated by

this modification; it is also possible to use stronger acids than are there indicated without risk of the formation of resinous compounds. This method is especially applicable to processes in which acetylene is introduced into hot solutions of mercury salts, so that the aldehyde distils as soon as it is formed. C. S.

Condensation and Similar Reactions and Method of Producing the Same. H. HIBBERT (Brit. Pat. 5408 of 1914; from *J. Soc. Chem. Ind.*, 1914, **33**, 984).—Iodine is used as a condensing agent to effect intramolecular condensation. The reaction may be carried out under diminished pressure. Mesityl oxide is obtained almost quantitatively by distilling diacetone alcohol [β-methylpentan-δ-ol-β-one] with about 0·0001% of its weight of iodine. Similarly, pinacone is converted into βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene, using 0·002% of iodine, and *cyclo*hexanol into *cyclo*hexene, using 0·02% of iodine. C. S.

Conversion of Lævulose into Mannitol by Hydrogenation. T. LUPIERI and H. MAYER (Fr. Pat. 468920; from *J. Soc. Chem. Ind.*, 1914, **33**, 977).—Lævulose is hydrogenated (i) by electrolysing a solution of the sugar in dilute sulphuric acid or alkali between inert electrodes, (ii) by hydrogen at a pressure of at least 3 atmo. in the presence of finely divided metals or metallic oxides at a temperature not exceeding 70°, (iii) by nascent hydrogen produced by the action of rhodium black or other finely divided, allied metals on formic acid, and (iv) continuously, by the action of sodium amalgam produced electrolytically. C. S.

The Phosphorus Content of Starch. A. W. THOMAS (*Biochem. Bull.*, 1914, **3**, 403—406).—The evidence of the present analyses is considered to support the view that the phosphorus in preparations of starch is not due to admixture with ash, but is in chemical combination. W. D. H.

Preparation of New Compounds [Derivatives of Aurothiosulphuric Acid] Suitable as Therapeutic Agents in the Treatment of Tuberculosis and Syphilis. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (Brit. Pat. 1869 of 1914; from *J. Soc. Chem. Ind.*, 1914, **33**, 806).—Aurothiosulphates of organic bases are obtained by allowing the latter or their salts to react with aurothiosulphuric acid or its salts. The *ethylenediamine* compound is a white, crystalline powder, which is easily soluble in water, but dissolves sparingly in alcohol. C. S.

Preparation of Hexamethylenetetramine Di-iodide. M. RIX (D.R.-P. 275974; from *J. Soc. Chem. Ind.*, 1914, **33**, 943).—An antiseptic compound of hexamethylenetetramine with iodine is obtained by the action of an aqueous solution of the base on a solution of iodine in an organic solvent which is immiscible with water, such as benzene or carbon tetrachloride. Antiseptic gauze may be prepared by impregnating the fabric with hexamethylenetetramine solution and then immersing it in the iodine solution. T. H. P.

Preparation of Hexamethylenetetramine Methyl Borate. K. H. SCHMITZ (D.R.-P. 275092; from *J. Soc. Chem. Ind.*, 1914, **33**, 807. Compare A., 1914, i, 20).—*Hexamethylenetetramine methyl borate*, $C_6H_{12}N_4$,Me·OH,5HBO_2, is obtained by: (1) heating hexamethylenetetramine with boric acid or methyl borate, with or without addition of either formaldehyde or a mixture of ammonia solution with formaldehyde or its polymerides, or (2) prolonged boiling of an aqueous solution of hexamethylenetetramine borate. It is far more stable than hexamethylenetetramine borate and finds medicinal use.

T. H. P.

Preparation of Hexamethylenetetramine Methyl Thiocyanate. K. H. SCHMITZ (Fr. Pat. 466619 [1st. Add.]; from *J. Soc. Chem. Ind.*, 1914, **33**, 845).—A double compound of hexamethylenetetramine and methyl thiocyanate, useful for medicinal purposes, is obtained as follows. A solution of formaldehyde and ammonia or of hexamethylenetetramine is treated with the methylamine or ammonium salt of an inorganic or organic acid, or a solution of a salt of hexamethylenetetramine is heated, with or without the addition of formaldehyde. In either case, a soluble thiocyanate is added, whereon hexamethylenetetramine methyl thiocyanate is separated. Another process consists in treating a solution of formaldehyde and ammonia or of hexamethylenetetramine with thiocyanic acid or its ammonium or methylamine salt, or a solution of hexamethylenetetramine thiocyanate is heated, with or without the addition of formaldehyde. In either of the above processes, the formaldehyde may be replaced by one of its polymerides.

The perchlorate, chromate, and other salts can be obtained in a similar manner to the thiocyanate. The free base, $C_6H_{12}N_4$,MeOH, is obtained by treating the chromate with barium oxide, or a haloid salt with moist silver oxide. Pure salts can be prepared by neutralising the base with the appropriate acid.

C. S.

Preparation of Alkyl- and Aryl-aminomethyl Alkyl Ethers. E. MERCK (D.R.-P. 273323; from *J. Soc. Chem. Ind.*, 1914, **33**, 668).—The interaction of a halogenated-methyl alkyl ether (1 mol.) and an aliphatic or aliphatic-aromatic primary or secondary amine (2 mols.), preferably in the presence of an indifferent organic solvent, yields products having the general formula $NRR^1{\cdot}CH_2{\cdot}OR^2$, where R represents an alkyl or arylalkyl radicle, R^1 hydrogen or an alkyl radicle, and R^2 an alkyl radicle. These compounds may be used in the preparation of medicinal products, such as hydrastinine.

T. H. P.

β-Acetylalkylenetetra alkyldiamines. FARBENFABRIKEN VORM FRIEDRICH BAYER & Co. (U.S. Pat. 1101754; from *J. Soc. Chem. Ind.*, 1914, **33**, 889—890).—Derivatives of αγ-diaminopropane of the type $CRAc(CH_2{\cdot}NR'_2)_2$, where R is H or an alkyl group, and R′ an alkyl group, are colourless, odourless oils, which are soluble in water and are valuable intermediate products for making erythrene or its homologues. They are prepared by the two-fold introduction of the group

·CH_2·NR'_2 into the corresponding ketone, and are separated from the monoamines by fractional distillation. *αγ-Bisdiethylamino-β-acetyl-β-methylpropane*, $CMeAc(CH_2 \cdot NEt_2)_2$, b. p. 105—110°/7—8 mm., is obtained by adding gradually 292 parts of a 50% aqueous solution of diethylamine to 75 parts of 40% aqueous formaldehyde, followed by 210 parts of methyl ethyl ketone, and boiling the mixture under a reflux condenser for several hours until a test portion, after being acidified with acetic acid, does not become turbid after the addition of a solution of aniline acetate. The solution is dehydrated over potassium hydroxide, the excess of the ketone is removed by distillation in a vacuum, and the residual mixture of bases is separated by fractional distillation in a vacuum.

αγ-Bisdiethylamino-β-acetylpropane, b. p. 90—110°/7—8 mm., is prepared in a similar manner. C. S.

Preparation of Derivatives of Bromodialkylacetamide. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 273320; from *J. Soc. Chem. Ind.*, 1914, **33**, 668).—When treated with formaldehyde in presence of a condensing agent, bromodialkylacetamides yield *N*-methylol compounds of the composition CRR'Br·CO·NH·CH_2·OH, where R and R' represent alkyl groups. These products possess marked hypnotic and sedative properties. T. H. P.

Preparation of α-Bromo*iso*valerylcarbamide. Knoll & Co. (D.R.-P. 275200; from *J. Soc. Chem. Ind.*, 1914, **33**, 806).—Treatment of an α-bromo*iso*valeryl haloid with a metallic cyanate in presence of an indifferent diluent gives α-bromo*iso*valeryl cyanate, which is converted into α-bromo*iso*valerylcarbamide by the action of ammonia. Carbimides are nearly always obtained in quantitative yield when acyl haloids are treated, in presence of a diluent, with silver or mercury *iso*cyanate; the latter is prepared from mercurous nitrate and potassium cyanate. T. H. P.

Diethylacetyl *iso*Cyanate [α-Ethylbutyrylcarbimide]. Synthetic Patents Co. (U.S. Pat. 1098938; from *J. Soc. Chem. Ind.*, 1914, **33**, 889).—*α-Ethylbutyrylcarbimide*, $CHEt_2 \cdot CO \cdot N:CO$, b. p. 67—72°/50 mm., prepared by treating α-ethylbutyryl chloride or bromide with silver or mercury *iso*cyanate, is a limpid oil which is soluble in benzene and light petroleum and yields α-ethylbutyrylcarbamide by treatment with ammonia. C. S.

Bromodiethylacetyl *iso*Cyanate [α-Bromo-α-ethylbutyrylcarbimide]. Farbenfabriken vorm. Friedrich Bayer & Co. (U.S. Pat. 1086294; from *J. Soc. Chem. Ind.*, 1914, **33**, 439).—*α-Bromo-α-ethylbutyrylcarbimide*, b. p. 110—114°/70 mm., is a limpid oil which is soluble in light petroleum and benzene. It is obtained by treating α-bromo-α-ethylbutyryl bromide or chloride with silver or mercury *iso*cyanate. It is converted by ammonia into α-bromo-α-ethylbutyrylcarbamide. C. S.

Preparation of Derivatives of Cyanohydrins of Aldehydes or Ketones. A. Albert (D.R.-P. 273073, 275442 and 275847; from *J. Soc. Chem. Ind*, 1914, **33**, 667, 890, 985).—Cyanohydrins of alde-

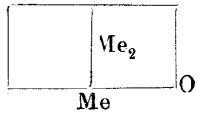
hydes or ketones are converted into acyl derivatives and these treated with hydrogen selenide in presence of an alcohol, the resulting compounds being esters of selenamidines. Thus the compound

$$CH_3\cdot CO_2\cdot CMe_2\cdot C(:NH)\cdot SeEt$$

is obtained by treating the cyanohydrin of acetylacetone with hydrogen selenide and ethyl alcohol. The acylated cyanohydrins may be replaced by aryl derivatives of aminonitriles; for instance, treatment of an alcoholic solution of *α*-acetylamino*iso*butyronitrile with a small proportion of alcoholic ammonia solution and saturation of the liquid with hydrogen selenide yields a selenamide of the structure

$$NHAc\cdot CMe_2\cdot CS\cdot NH_2.$$ T. H. P.

Simplified Representation of Cyclic Compounds. Enrique V. Zappi (*Anal. Soc. Quim. Argentina*, 1914, **2**, 119—123).—The author proposes to use the simple hexagon as the formula of *cyclo*hexane instead of for benzene, as is usually done. In benzene, alternating double linkings are represented. The formula suggested, for instance for camphor, is



G. D. L.

Substitution in the Benzene Nucleus. A. F. Holleman (*J. Amer. Chem. Soc.*, 1914, **36**, 2495—2498).—Several objections are raised against the electronic hypothesis proposed by Fry (A., 1912, ii, 546; 1914, i, 263) to explain the phenomena of substitution in the benzene nucleus, and, in view of these, the author is of opinion that the hypothesis cannot be accepted. E. G.

Preparation of Unsaturated Organic Compounds. F. E. Matthews, H. J. W. Bliss, and H. M. Elder (Brit. Pat. 17234 of 1912 and 16828 of 1913; from *J. Soc. Chem. Ind.*, 1913, **32**, 884; 1914, **33**, 889).—The principal patent describes the method of eliminating hydrogen haloids from halogenated hydrocarbons by means of water or steam. It is now found that this process is also applicable to the removal of hydrogen haloid from other halogenated organic compounds. Such compounds are treated with steam at temperatures between 100° and 700°, with or without the use of a catalyst. In some cases it is advantageous to subject the mixed heated vapours to the action of the silent electric discharge or to ultra-violet light. For example, a suspension of 100 grams of *β*-bromo-*β*-phenylpropionic acid in water is introduced gradually into a silica tube at 600—650°. Hydrogen bromide and carbon dioxide are eliminated, and the styrene formed is isolated by distillation with steam and fractionation. The unchanged *β*-bromo-*β*-phenylpropionic acid is recovered and again passed through the silica tube. C. S.

Preparation of Chlorinated Cyclic Compounds. Fabriques de Produits de Chimie Organique de Laire (Fr. Pat. 464645; Brit. Pat. 30068 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 503).—Benzyl chloride and its homologues are obtained by condensing

aromatic hydrocarbons with chloroacetone in the presence of stannic chloride or other suitable metallic chloride. When homologues of benzene are used, the chloromethyl group generally enters the benzene nucleus in the para-position to the alkyl group. The methyl, ethyl, propyl, butyl, amyl, *cyclo*hexyl, methylethyl, methylpropyl, and methylbutyl derivatives of benzyl chloride have been prepared by this method. For example, equal molecular proportions of toluene and chloroacetone are dissolved in twice their weight of carbon disulphide or carbon tetrachloride, the solution is cooled to about −10°, and 0·25 mol. of stannic chloride is added drop by drop. After keeping the mixture for half an hour, the oil is separated, poured on ice, washed with water, and distilled; after unchanged toluene has been removed, *w*-chloro-*p*-xylene distils at 102—110°/30 mm. The yield is about 60% of the toluene used. C. S.

Direct Reduction of Aromatic Nitro-compounds to Nitroso-compounds. I. J. RINKES (*Chem. Weekblad*, 1914, **11**, 1062—1064).—When heated with reduced iron at 200—230° in an atmosphere of carbon dioxide, nitrobenzene, *p*-fluoronitrobenzene, and *p*-chloronitrobenzene give a poor yield of the corresponding nitroso-compound, varying between 2·5 and 9%. A. J. W.

[**Aminophenylselenic Acid, etc.**] H. S. WELLCOME and F. L. PYMAN (Brit. Pat. 2787 of 1914; from *J. Soc. Chem. Ind.*, 1914, **33**, 889).—Phenylseleninic acid or its nitrate is converted by nitration with sulphuric acid and potassium nitrate into a *nitrophenylselenious acid*, $NO_2 \cdot C_6H_4 \cdot SeO_2H$, m. p. 156—157°. This is converted by reduction with sodium hydrogen sulphite into a *dinitrodiphenyl diselenide*, $Se_2(C_6H_4 \cdot NO_2)_2$, m. p. 83°, which is further reduced by sodium sulphide to *diaminodiphenyl diselenide* (crystalline *hydrochloride*, m. p. 291—292°). The *acetyl* derivative, m. p. 185—186°, of the latter is obtained by means of acetic anhydride, and is oxidised by nitric acid to *acetylaminophenylselenious acid*, m. p. 209°. The last substance is converted by alkaline potassium permanganate into salts of *acetylaminophenylselenic acid*. The free acid is converted into *aminophenylselenic acid*, $NH_2 \cdot C_6H_4 \cdot SeO_3H$, m. p. 229°, by boiling with water. The selenic acid and its salts, which are crystalline, are said to possess valuable physiological properties. C. S.

Preparation of Anthracene Derivatives. M. KARDOS (D.R.-P. 275248; from *J. Soc. Chem. Ind.*, 1914, **33**, 826).—Treatment of anthracene or one of its derivatives with malonyl chloride in presence of a substance which assists condensation, yields coloured compounds which are probably 1 : 9-malonylanthracene derivatives and are converted into anthraquinone-1-carboxylic acid or its derivatives by mild oxidation, for instance, by means of permanganate, in alkaline solution. T. H. P.

Preparation of Derivatives of Acetoacetanilide. FARBENFABRIK VORM. F. BAYER & Co. (D.R.-P. 273321; from *J. Soc. Chem. Ind.*, 1914, **33**, 637).—Esters of *p*-acetoacetylaminobenzoic acid are

obtained in good yield by heating *p*-aminobenzoic esters with ethyl acetoacetate, either alone or in presence of a diluent, but when the isomeric aminobenzoic esters are used, the reaction is very incomplete. T. H. P.

Preparation of Acyl Derivatives of *p*-Phenetidine. P. BERGELL (D.R.-P. 277022; from *J. Soc. Chem. Ind.*, 1914, **33**, 1115).—*α-Bromo-isovaleryl-p-phenetidine*, m. p. 151°, prepared, for example, by treating the base with bromo*iso*valeryl bromide in presence of benzene, exhibits the physiological properties of its components. T. H. P.

Preparation of α-Bromo*iso*valeryl-*p*-phenetidine. J. D. RIEDEL (U.S. Pat. 1094296; from *J. Soc. Chem. Ind.*, 1914, **33**, 567).—α Bromo*iso*valeryl bromide is added slowly, with stirring, to *p*-phenetidine in benzene, and the liquid is heated, filtered, and allowed to cool. *α-Bromoisovaleryl-p-phenetidine*, m. p. 151°, thus obtained, is sparingly soluble in water, dissolves readily in alcohol, ether, or benzene, and is slowly decomposed by alcoholic alkali hydroxides. It has soporific and strong anti-neuralgic properties. C. S.

Preparation of Alkyloxyaryl-, Dialkyloxyaryl-, and Alkylenedioxyaryl-aminopropanes or their *N*-Monoalkyl Derivatives. E. MERCK (D.R.-P. 274350; from *J. Soc. Chem. Ind.*, 1914, **33**, 807).—Unsaturated propylene compounds of the general formula

$$CH_2R{\cdot}CH{:}CH_2 \text{ or } CHR{:}CHMe,$$

where R is an alkyloxyaryl, dialkyloxyaryl or alkylenedioxyaryl radicle, are treated with hydrogen haloids and the products subjected to the action of ammonia or a primary aromatic amine. In the first stage of the reaction, the halogen atom unites with the unsaturated carbon atom nearest to the benzene nucleus. T. H. P.

***p*-Nitrosophenylglycine.** J. D. RIEDEL (Brit. Pat. 22694 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 70. Compare A., 1913, i, 469).—*p*-Nitrosophenylglycine is obtained directly, and in good yield, from commercial phenylglycine by treatment with a nitrite, nitrous acid, or nitrosyl chloride in the presence of fuming hydrochloric acid. The nitrosoamine of phenylglycine or its esters is not converted into the *p*-nitroso-compound by alcoholic hydrochloric acid according to Fischer and Hepp's process. *p*-Nitrosophenylglycine is a brown powder, practically insoluble in ether, alcohol, and water. It is soluble in aqueous ammonia, forming a stable, deep green solution from which intensely green crystals of the ammonium salt are precipitated by alcohol. C. S.

Preparation of *p*-Nitrophenylcarbamyl Chloride (and Diarylcarbamides). FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (Fr. Pat. 459885 [1st Add.]; Brit. Pat. 17123 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 219).—*p*-Nitrophenylcarbamyl chloride, described in the principal patent, is treated with a primary or secondary base or a substitution product thereof (sulphonic acid, hydroxysulphonic acid, etc.), with or without the addition of a substance to neutralise the

hydrogen chloride produced. Di-*p*-nitrophenylcarbamide is formed when *p*-nitroaniline is used as the base. The product can be obtained in one operation by treating with carbonyl chloride 2 mol. of the same base or 1 mol. each of two different bases. C. S.

Preparation of Diarylcarbamyl Chlorides. BADISCHE ANILIN- & SODA-FABRIK (Brit. Pat. 20107 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 825).—Diarylamines can be converted completely into the corresponding diarylcarbamyl chlorides, free or practically free from diarylamine hydrochloride, by carrying out the last part of the treatment with carbonyl chloride at a higher temperature, for example, 100°, and continuing the reaction until all the diarylamine hydrochloride has been converted into the carbamyl chloride. The operation may be performed either with or without a solvent or diluent. C. S.

Molecular Transposition in the *cyclo*Hexane Series; Passage to the *cyclo*Pentane Series. M. TIFFENEAU (*Compt. rend.*, 1914, **159**, 771—774. Compare de Rességuier, A., 1914, i, 528).—The iodohydrin of *cyclo*hexanediol when treated with silver nitrate yields *cyclo*pentanal, the ring being opened and closing on a new carbon atom. 2-Iodo-4-methyl*cyclo*hexan-1-ol similarly yields 3-methyl*cyclo*pentan-1-al. This result points to the constitution of the iodo-derivative as being represented by formula I and not by formula II:

$$CHMe\begin{<}{CH_2\cdot CHI \atop CH_2-CH_2}\end{>}CH\cdot OH \qquad CHMe\begin{<}{CH_2\cdot CH(OH) \atop CH_2\text{——}CH_2}\end{>}CHI.$$

(I.) (II.)

The iodohydrins derived from the oxides of 3-methyl*cyclo*hexene and 2-methyl*cyclo*hexene yielded with silver nitrate 2-methyl*cyclo*pentan-1-al and *cyclo*pentanyl methyl ketone respectively. W. G.

Molecular Transposition in the Phenyl*cyclo*hexane Series: Migration of the Phenyl Group without Passage to the *cyclo*Pentane Series. MARCEL LE BRAZIDEC (*Compt. rend.*, 1914, **159**, 774—777. Compare Tiffeneau, preceding abstract).—2-Iodo-1-phenyl*cyclo*hexan-1-ol reacts with silver nitrate, losing the elements of hydrogen iodide and giving 1-*phenyl*cyclo*hexan*-2-*one*, m. p. 63°, yielding a *semicarbazone*, m. p. 196°. On oxidation it yields δ-benzoylvaleric acid. 2-Iodo-1-phenyl-4-methyl*cyclo*hexan-1-ol similarly yields 1-*phenyl*-3-*methyl*cyclo*hexan*-6-*one*, needles, m. p. 64°, giving a *semicarbazone*, m. p. 219°. On oxidation this ketone yields first δ-*benzoyl*-γ-*methylvaleric acid*, m. p. 55°, giving a *semicarbazone*, m. p. 215°, and then benzoic acid and α-methylglutaric acid. The intermediate products in the formation of these ketones should be vinyl alcohols and these have been isolated and characterised.

1-*Phenyl*-Δ¹-cyclo*hexen*-2-*ol*, $OH\cdot C\begin{<}{CPh\cdot CH_2 \atop CH_2\cdot CH_2}\end{>}CH_2$, crystallises in needles, m. p. 94°, giving an *acetyl* derivative, m. p. 114°. 1-*Phenyl*-5-*methyl*-Δ¹-cyclo*hexen*-2-*ol* has m. p. 120°. These two alcohols on warming with dilute acids yield the corresponding ketones, but the reverse process by boiling the ketones with acetic anhydride does not yield the vinyl acetates. W. G.

Preparation of Pure, Stable Salts of *p*-Dimethylaminophenol and of *p*-Hydroxyphenyltrimethylammonium Hydroxide. FABRIQUE DE PRODUITS CHIMIQUE CI-DEV. SANDOZ (Fr. Pat. 467085; Brit. Pat. 20736 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 845).—The product obtained by the methylation of *p*-aminophenol contains methyl- and dimethyl-aminophenols and a salt of *p*-hydroxyphenyltrimethylammonium hydroxide. To separate these, advantage is taken of the fact that *p*-aminophenol and *p*-methylaminophenol do not form precipitates with ferrocyanides in acid solution, whilst the other two compounds are precipitated rapidly and completely as acid ferrocyanides; these two compounds can then be separated from one another by recrystallisation in the presence of an alkali sulphite, whereby *p*-dimethylaminophenol is separated in the form of a normal ferrocyanide, whilst the quaternary ammonium compound remains in the solution.

A separation of the bases from the mixture of the ferrocyanides is also effected by faintly basifying the mixture and extracting the *p*-dimethylaminophenol by benzene or other solvent. C. S.

Preparation of Esters of Homologues of Phenol Containing Halogen in the Side Chain. SCHMITZ & Co. (Brit. Pat. 3053 of 1914; Fr. Pat. 468363; from *J. Soc. Chem. Ind.*, 1914, **33**, 767).—Halogens can be introduced into the side chains of esters of the homologues of phenol by treating the esters with halogens or their equivalent in the presence of light, preferably from a source rich in ultra-violet rays, and at the ordinary temperature or below 100°. The esters are dissolved in carbon tetrachloride or other suitable solvent. In some cases it is advisable to use a halogen carrier. For example, the introduction of chlorine into a solution of *o*-tolyl carbonate in carbon tetrachloride at about 25—30° under the influence of the rays from a mercury vapour lamp produces ωω-dichloro-*o*-tolyl carbonate in the form of an oil. By chlorinating the solid tolyl carbonate in the presence of a small quantity of phosphorus pentachloride, ωωω-trichloro-*o*-tolyl carbonate is produced. C. S.

Preparation of *C*-Allylphenols and their Analogues and of *C*-Propenylphenolcarboxylic Acids and their Nucleus-substitution Products. L. CLAISEN (D.R.-P. 268099 and 268982, and Brit. Pat. 24932 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 220, 277).—Allyl ethers of phenols, or their analogues or nucleus-substitution products, may be converted into the corresponding allyl derivatives of the phenols by heating at high temperatures, the allyl group assuming the ortho- or para-position with respect to the hydroxyl group. The allyl derivatives of phenolcarboxylic acids, prepared in this way, are transformed into the corresponding propenyl derivatives when heated with alkali hydroxides. T. H. P.

Preparation of Aromatic Hydroxy-derivatives. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (Fr. Pat. 469040; from *J. Soc. Chem. Ind.*, 1914, **33**, 955).—The formation of oxidation products, which always occurs when aromatic sulphonic acids are fused with

alkali hydroxides, can be avoided if the two substances are heated together in aqueous solution at high temperatures, for example, 300°. A mixture of sodium naphthalene-β-sulphonate (46 parts) and 50 parts of sodium hydroxide (D 1·383) is heated at 300—330° in a closed vessel for ten to twenty hours. The cooled mass is acidified and the β-naphthol is filtered, washed, and dried. The yield is good and the β-naphthol is only very slightly coloured. C. S.

Preparation of Carbamides of the Naphthalene Series. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (Brit. Pat. 9472 of 1914; from *J. Soc. Chem. Ind.*, 1914, **33**, 825—826).—New carbamides of the naphthalene series, suitable for medicinal purposes and for the production of substantive cotton dyes, are obtained by treating with carbonyl chloride derivatives of 8-amino-α-naphtholsulphonic acids, which are substituted in the amino-group by the aminobenzoyl or aminobenzoylaminobenzoyl group or their derivatives, or by a number of similarly grouped aminobenzoyl residues or their derivatives. The *compound* produced by the action of carbonyl chloride on 8-*p*-aminobenzoylamino-α-naphthol-3 : 5-disulphonic acid has a strong curative effect on animals affected with trypanosomes, and by reacting with a benzenediazonium salt yields a pure bluish-red dye. C. S.

Preparation of Catechol-4 : 6-disulphonic Acid. SACCHARINFABRIK VORM. FAHLBERG, LIST & Co. (D.R.-P. 276273; from *J. Soc. Chem. Ind.*, 1914, **33**, 1044).—The *o*-halogenated phenoldisulphonic acid, obtained by treating phenol-2 : 4-disulphonic acid with chlorine or bromine in acid solution, is converted into catechol-4 : 6-disulphonic acid by heating with dilute alkali solution under pressure at below 200°. T. H. P.

Preparation of Benzyl Alcohol. F. W. KLEVER (Fr. Pat. 462438; from *J. Soc. Chem. Ind.*, 1914, **33**, 277).—Benzyl chloride is converted quantitatively into benzyl alcohol by heating it, in the presence of an excess of water, with magnesium hydroxide, a hydroxide of an alkaline earth metal, zinc hydroxide, or other basic hydroxide excepting that of lead, the mixture being thoroughly agitated during the process. By heating 1 mol. of benzyl chloride with 0·6 mol. of magnesium hydroxide and 8—10 times the theoretical amount of water at 100°, benzyl alcohol is obtained in 96% yield. The yield is somewhat less when calcium hydroxide is used. C. S.

Preparation of Benzyl Esters of Lower Fatty Acids and of Benzyl Alcohol from Benzyl Chloride. F. W. KLEVER (Fr. Pat. 462439; from *J. Soc. Chem. Ind.*, 1914, **33**, 277).—Benzyl esters of the lower fatty acids are obtained in good yield by heating a mixture of benzyl chloride and an anhydrous salt of the acid in the presence of a small quantity, 0·1—1 mol., of the acid itself, the presence of water being avoided. For example, benzyl chloride (1 mol.), anhydrous sodium acetate (1·1—1·2 mol.), and glacial acetic acid (0·1—1 mol.) yield benzyl acetate. The mixture obtained by this method may be heated with water until the odour of the acetate is not perceptible, the liquid neutralised, and the benzyl alcohol separated.

Benzyl formate is prepared in a similar manner, using 1·25—1·5 mol. of anhydrous formic acid. C. S.

Preparation of 2-Dimethylamino-5-methylbenzyl Alcohol. L. CASSELLA & Co. (D.R.-P. 268486; from *J. Soc. Chem. Ind.*, 1914, **33**, 194).—Dimethyl-*p*-toluidine may be converted into 2-dimethylamino-5-methylbenzyl alcohol by treatment with a considerable excess of formaldehyde in presence of a mineral acid. It may be condensed to a diphenylmethane derivative by heating with a further quantity of dimethyl-*p*-toluidine or other tertiary aromatic base at a high temperature in presence of zinc chloride. T. H. P.

Additive Compounds of Organic Substances with Sulphuric Acid. JAMES KENDALL and CLIFFORD D. CARPENTER (*J. Amer. Chem. Soc.*, 1914, **36**, 2498—2517).—In earlier papers (A., 1914, i, 858, 1069), experiments have been described on the formation of additive compounds of certain substances with organic acids. The method used in these investigations has now been applied to the study of sulphonation. The substances are mixed at as low a temperature as possible and the mixture is frozen, and in this way additive compounds, if formed, are at once isolated. The results show that sulphonation is preceded by the formation of additive compounds of the nature of oxonium salts; this reaction is ionic and instantaneous.

Benzoic, *o*-, *m*- and *p*-toluic, phenylacetic, and crotonic acids yielded *compounds* of the type $R\cdot CO_2H,H_2SO_4$. Glutaric acid furnished the *compound*, $C_3H_6(CO_2H)_2,H_2SO_4$, and *m*-toluic acid furnished a second *compound*, $2C_7H_7\cdot CO_2H,H_2SO_4$. Phenol gave the *compound*,

$$2C_6H_5\cdot OH,H_2SO_4;$$

p-cresol, the *compounds*, $2C_7H_7\cdot OH,H_2SO_4$ and $C_7H_7\cdot OH,2H_2SO_4$; *o*-xylenol, the *compounds*, $2C_8H_9\cdot OH,H_2SO_4$ and $C_8H_9\cdot OH,H_2SO_4$; *p*-xylenol, the *compounds*, $C_8H_9\cdot OH,H_2SO_4$ and $C_8H_9\cdot OH,2H_2SO_4$; *m*- and *p*-nitrophenol furnished *compounds* of the formula

$$2C_6H_4(NO_2)\cdot OH,H_2SO_4.$$

Acetophenone yielded the *compound*, $2CH_3\cdot CO\cdot C_6H_5,H_2SO_4$; benzophenone, the *compound*, $C_6H_5\cdot CO\cdot C_6H_5,H_2SO_4$; dimethylpyrone, the *compounds*, $2C_7H_8O_2,H_2SO_4$, $C_7H_8O_2,H_2SO_4$, and $2C_7H_8O_2,3H_2SO_4$; benzoic anhydride, the *compounds*, $2C_{14}H_{10}O_3,H_2SO_4$, $C_{14}H_{10}O_3,H_2SO_4$, and $C_{14}H_{10}O_3,2H_2SO_4$; and coumarin, the *compound*, $C_9H_6O_2,H_2SO_4$. E. G.

Preparation of Derivatives of *p*-Aminophenyl Salicylate containing Sulphur. J. ABELIN, E. BÜRGI, and M. PERELSTEIN (D.R.-P. 273221; from *J. Soc. Chem. Ind.*, 1914, **33**, 667. Compare A., 1914, i, 283).—*p*-Aminophenyl salicylate is treated with an alkali or ammonium salt of methane-, ethane- or propane-sulphonic acid in presence of methyl or ethyl alcohol and, preferably, in presence of a condensing agent, such as sodium acetate. The alkylsulphonates are obtained pure and in almost quantitative yield. T. H. P.

Preparation of Carbamide *o*-Acetoxybenzoate. SCHÜTZ & Co. (D.R.-P. 274046; from *J. Soc. Chem. Ind.*, 1914, **33**, 806).—When

o-acetoxybenzoic acid (1 mol.) and carbamide (1 mol.) are dissolved in concentrated alcohol or other suitable solvent at 60° and the combined solutions are evaporated at as low a temperature as possible, preferably in a vacuum, the product consists of pure carbamide *o*-acetoxybenzoate, uncontaminated with the salicylate and possesses antirheumatic, analgesic and antiuric properties. T. H. P.

Preparation of α-Bromo*iso*valerylcarbamide *o*-Acetoxybenzoate. KNOLL & Co (D.R.-P. 274349; from *J. Soc. Chem. Ind.*, 1914, **33**, 806).—This compound, prepared by melting *o*-acetoxybenzoic acid (1 mol.) with α-bromo*iso*valerylcarbamide (1 mol.), with or without a solvent, exhibits the sedative properties of carbamide and all the characteristics of compounds of salicylic acid, but is free from the sudorific effects attending the administration of *o*-acetoxybenzoic acid. T. H. P.

Preparation of Compounds Containing Derivatives of Sulphosalicylic Acid. FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (Fr. Pat. 466236; Brit. Pat. 22854 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 637).—The sulphonyl chlorides of aromatic *o*-hydroxycarboxylic acids are condensed with ammonia, amines, aminophenols, aminonaphthols, or their sulphonic or carboxylic acids or other derivatives. For example, salicylic acid *p*-sulphonamide, $CO_2H \cdot C_6H_3(OH) \cdot SO_2 \cdot NH_2$, is obtained by the action of aqueous ammonia on the sulphonyl chloride of salicylic acid. The products may be used in the preparation of dyes. C. S.

Sulphonyl Chlorides of Nitrated *o*-Hydroxycarboxylic Acids or their Derivatives. FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (Brit. Pat. 12061 of 1914; from *J. Soc. Chem. Ind.*, 1914, **33**, 855).—Sulphonyl chlorides of phenyl-*o*-carboxylic acids or their derivatives can be nitrated in the usual manner. The 5-sulphonyl chloride of salicylic acid is converted into 3-nitro-2-hydroxybenzoic acid-5-sulphonyl chloride. The products may be used as intermediate compounds in the manufacture of azo-dyes. C. S.

Preparation of 6-Chloro-3-hydroxy-*p*-toluic Acid. J. D. RIEDEL (D.R.-P. 275093; from *J. Soc. Chem. Ind.*, 1914, **33**, 807).—*6-Chloro-3-hydroxy-*p*-toluic acid* is obtained in almost quantitative yield when the sodium derivative of 6-chloro-*m*-cresol is heated, in presence of carbon dioxide, under pressure at a high temperature, preferably at 160—180°. Unlike 5-chlorosalicylic acid, which has not been found to possess therapeutic value, the new acid exhibits powerful antiseptic properties. T. H. P.

Preparation of [6-Halogen-3-hydroxy-*p*-toluic Acid]. J. D. RIEDEL (Fr. Pat. 468949; from *J. Soc. Chem. Ind.*, 1914, **33**, 984).—3-Hydroxy-*p*-toluic acid is converted into 6-halogen-3-hydroxy-*p*-toluic acids by treatment with the calculated amount of the halogen in the presence of carbon tetrachloride, glacial acetic acid, etc. The chlorinated acid has been described (preceding abstract). The acids

are powerful antiseptics. Their soluble salts, as well as those of other derivatives of salicylic acid and its homologues halogenated in the para-position to the hydroxyl group, also possess antiseptic properties.
C. S.

Preparation of Derivatives of *o*-Hydroxyallylbenzoic Acids. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 274047; from *J. Soc. Chem. Ind.*, 1914, **33**, 806).—When *o*-hydroxyallylbenzoic acids are treated with acylating agents and the acyl derivatives converted into salts, the latter possess antipyretic, antineuralgic and antirheumatic properties in more marked degree than the corresponding *o*-acyloxybenzoic acids. T. H. P.

Preparation of α-Amino-β-3 : 4-dihydroxyphenylpropionic Acid. F. HOFFMANN, LA ROCHE & Co. (D.R.-P. 275443; from *J. Soc. Chem. Ind.*, 1914, **33**, 943).—Extraction of the seeds or hulls of *Vicia faba* for a short time with aqueous sulphurous acid yields a liquid containing α-amino-β-3 : 4-dihydroxyphenylpropionic acid, which may be isolated by conversion into its insoluble lead compound and decomposition of the latter by means of sulphuric acid. The free acid, m. p. 280° (decomp.), $[\alpha]_D$ −18·91°, is sparingly soluble in cold, but more readily in hot, water, and, when heated, it loses carbon dioxide with formation of the corresponding dihydroxyphenylethylamine.
T. H. P.

Preparation of Arylamides of 2 : 3-Dihydroxynaphthoic Acid and Their Condensation Products with Formaldehyde. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (Brit. Pat. 23732 of 1913 and 3312 of 1914; Fr. Pat. 464478; U.S. Pat. 1101111; from *J. Soc. Chem. Ind.*, 1914, **33**, 70, 742).—Arylamides of 2 : 3-dihydroxynaphthoic acid are obtained by heating the acid with a non-nitrated arylamine in the presence of a dehydrating agent and an indifferent solvent or suspending medium. The preparation of the anilide, 2 : 5-dichloroanilide, and β-naphthalide, and of the compound with 2 : 4-tolylenediamine is described in detail.

Formaldehyde reacts very readily with arylamides of 2 : 3-dihydroxynaphthoic acid in alkaline solution, forming products which are precipitated by acids. The constitution of the new products has not been determined. They differ from the arylamides themselves in being less readily soluble, for example, in acetone, and they are decomposed by heat. They may be used as components of azo-dyes. C. S.

Preparation of Phthaleins of the Naphthalene Series. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 275897; from *J. Soc. Chem. Ind.*, 1914, **33**, 957).—1 : 6-Dihydroxynaphthalene is combined with phthalic anhydride or its substitution products, with or without addition of a condensing agent, for example, by heating on an oil-bath at 180—200°. The dark red compounds obtained are soluble in alkali and act as deep, bluish-green dyes. T. H. P.

Indenedicarboxylic Acid and Hydrindenedicarboxylic Acid. J. BOUGAULT (*Compt. rend.*, 1914, **159**, 745—747).—Ethyl phenyloxalacetate with concentrated sulphuric acid is simply hydrolysed and dehydr-

ated, giving the anhydride of phenylhydroxymaleic acid. Its next higher homologue, however, benzyloxalacetic ester behaves differently, giving *diethyl indenedicarboxylate*, $\begin{matrix}C_6H_4\cdot C\cdot CO_2Et\\ \vert\quad\quad\Vert\\ CH_2\text{--}C\cdot CO_2Et\end{matrix}$, voluminous crystals, m. p. 78°, which on saponification with alkali yields ethyl alcohol, carbon dioxide, and indenecarboxylic acid (compare Perkin and Revay, T., 1894, **65**, 231). Hydrolysis with acid, however, gives *indenedicarboxylic acid*, $\begin{matrix}C_6H_4\cdot C\cdot CO_2H\\ \vert\quad\quad\Vert\\ CH_2\text{--}C\cdot CO_2H\end{matrix}$, which is almost insoluble in ether, benzene, and acetic acid, more readily soluble in alcohol or acetone. It decomposes at 215°, giving carbon dioxide and indenecarboxylic acid. Esterification with ethyl iodide only yields the ester of the latter acid, but on warming with alcohol saturated with hydrogen chloride, indenedicarboxylic acid gives its own diethyl ester. The free acid on reduction with zinc in acetic acid yields *hydrindenedicarboxylic acid*, $\begin{matrix}C_6H_4\cdot CH\cdot CO_2H\\ \vert\quad\quad\vert\\ CH_2\text{--}CH\cdot CO_2H\end{matrix}$, m. p. 222°, which is more soluble and more stable than indenedicarboxylic acid. W. G.

Preparation of Anthraquinone Nitriles. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 27179 and 275517; from *J. Soc. Chem. Ind.*, 1914, **33**, 637, 826).—Anthraquinone-α- or -β-nitrile is obtained by heating α- or β-halogenated anthraquinones with copper cyanide in presence of an indifferent solvent and may be used for the preparation of colouring matters. T. H. P.

Preparation of Quinizarin-β-carboxylic Acid. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 273341; from *J. Soc. Chem. Ind.*, 1914, **33**, 784).—The methyl group of β-methylquinizarin is oxidised to the carboxyl group by treatment with nitrosylsulphuric acid in sulphuric acid solution, preferably in presence of boric acid; the quinizarin-β-carboxylic acid may be used as a lake or mordant colouring matter. T. H. P.

Preparation of Purpurincarboxylic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 272301; Brit. Pat. 22980 of 1913; 1st addition to Fr. Pat. 451927; from *J. Soc. Chem. Ind.*, 1914, **33**, 545).—1 : 4-Dihydroxyanthraquinone-3-carboxylic acid is used in place of the isomeric 1 : 2-dihydroxy-acid of the principal patent (compare A., 1913, i, 1197). The first product of the oxidation appears to be 2-hydroxyanthradiquinone-3-carboxylic acid, and this, on prolongation of the fusion, or addition of a reducing agent or introduction of the fused mass into aqueous metal hydrogen sulphite solution, is converted into 1 : 2 : 4-trihydroxyanthraquinone-3-carboxylic acid. T. H. P.

Preparation of Basic Bismuth Gallocarboxylate. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 276072; from *J. Soc. Chem. Ind.*, 1914, **33**, 890).—A salt identical with that previously described (compare A., 1914, i, 694) is obtained by the action of a basic bismuth salt or bismuth hydroxide on gallocarboxylic acid in presence of alkali. T. H. P.

Conversion of Haloid Derivatives into Aldehydes. FABRIQUES DE PRODUITS DE CHIMIE ORGANIQUE DE LAIRE (Fr. Pat. 452537 [1st. Add.]; from *J. Soc. Chem. Ind.*, 1914, **33**, 667. Compare *ibid.*, 1913, **32**, 673).—A number of new aldehydes have been obtained by the action of urotropine (hexamethylenetetramine) on monohaloid derivatives, as described in the principal patent. Among them are *m*- and *p*-tolualdehydes, 3 : 4-, 2 : 4-, and 2 : 5-dimethylbenzaldehydes, *p*-ethyl-, *p*-propyl-, *p*-butyl-, *p-iso*amyl-, and *p-cyclo*hexyl-benzaldehydes, and methylethyl-, methylpropyl-, and methylbutyl-benzaldehydes. Mixed carbonates, such as ω-chlorotolyl ethyl carbonate,

$$CH_2Cl\cdot C_6H_4\cdot O\cdot CO_2Et,$$

may also be employed for the preparation of hydroxyaldehydes.

C. S.

New Compound [3 : 3′-Dinitro-4 : 4′-diaminobenzophenone] Suitable for Use in the Preparation of Pigments. BADISCHE ANILIN-UND SODA-FABRIK (Brit. Pat. 8690 of 1914; U. S. Pat. 1104611; from *J. Soc. Chem. Ind.*, 1914, **33**, 743).—4 : 4′-Dichlorobenzophenone is nitrated and the product is heated for ten hours at 150—160° with alcoholic ammonia containing 10% of ammonia. The *product*, after crystallisation from *m*-cresol, has m. p. 292°, and is considered to be 3 : 3′-*dinitro*-4 : 4′-*diaminobenzophenone*; it differs materially from the compound, m. p. 121°, obtained by Consonno by nitrating diaminobenzophenone. When 10% aqueous ammonia is employed, the diamino-compound is obtained mixed with 4-chloro-3 : 3′-dinitro-4′-aminobenzophenone.

C. S.

Chalkones and Hydrochalkones [Phenyl Styryl Ketones and Phenyl Phenylethyl Ketones]. V. G. BARGELLINI (*Gazzetta*, 1914, **44**, ii, 421—426. Compare A., 1914, i, 1074).—Reduction of 2-hydroxy-4 : 6-dimethoxyphenyl 4-methoxystyryl ketone and 2 : 4 : 6-trimethoxyphenyl 4-methoxystyryl ketone by means of hydrogen in presence of palladium black yields compounds differing from Ciamician and Silber's tri- and tetra-methylphloretin (A., 1895, i, 538), in which the methyl groups are attached, not to oxygen, but to the carbon atoms of the nuclei. Unsuccessful attempts were made to methylate phloretin by means of methyl sulphate, and the action of diazomethane on naringenin and phloretin is being studied. In the meantime, Franck (compare A., 1914, i, 1132) has succeeded in reducing naringenin to phloretin.

2-*Hydroxy*-4 : 6-*dimethoxyphenyl β*-4-*methoxyphenylethyl ketone*,

$$OH\cdot C_6H_2(OMe)_2\cdot CO\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot OMe,$$

forms white laminæ, m. p. 110—111°, and, in alcoholic solution, gives a reddish-brown coloration with ferric chloride.

2 : 4 : 6-*Trimethoxyphenyl* 4-*methoxystyryl ketone*,

$$C_6H_2(OMe)_3\cdot CO\cdot CH{:}CH\cdot C_6H_4\cdot OMe,$$

prepared by the interaction of anisaldehyde and 2 : 4 : 6-trimethoxyacetophenone in alcoholic solution in presence of sodium hydroxide, forms pale yellow scales, m. p. 119—121°, and dissolves in concentrated sulphuric acid with an orange-red coloration.

2 : 4 : 6-*Trimethoxyphenyl β*-4-*methoxyphenylethyl ketone*,

$$C_6H_2(OMe)_3\cdot CO\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot OMe,$$

was obtained only as an oil. Attempts to hydrolyse the methoxyl groups of this compound resulted in the formation, not of the corresponding tetrahydroxy-derivative, but of its products of decomposition. Thus, with hydriodic acid, β-*p*-hydroxyphenylpropionic acid was obtained, and with hydrobromic acid, (1) a bright red powder, m. p. about 260° (decomp.), (2) β-*p*-methoxyphenylpropionic acid, and (3) a small proportion of a compound exhibiting the melting point and reactions of phloroglucinol. Thus, the decomposition of 2 : 4 : 6-trimethoxyphenyl 4-methoxyphenylethyl ketone by these acids is analogous to that of phloretin by alkali. T. H. P.

Preparation of Anthraquinone. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (U.S. Pat. 1103383; from *J. Soc. Chem. Ind.*, 1914, **33**, 826).—Anthracene is treated with nitric acid below 60° in the presence of an indifferent liquid, and the intermediate compound is converted into anthraquinone by nitric acid above 60°. C. S.

Preparation of 1-Chloroanthraquinone and its Nitro- and Chloro-derivatives. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 267544 and 271681; from *J. Soc. Chem. Ind.*, 1914, **33**, 70, 544).—Treatment of anthraquinone-1-sulphonic acid or one of its salts with thionyl chloride at a high temperature results in the formation of the sulphonyl chloride, which loses sulphur dioxide and is converted into 1-chloroanthraquinone. When a nitroanthraquinonesulphonic or an anthraquinonedisulphonic acid or one of its salts is used, the corresponding chloronitro- or dichloro-anthraquinone is obtained. T. H. P.

Preparation of Aminoanthraquinones. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (U.S. Pat. 1104943; from *J. Soc. Chem. Ind.*, 1914, **33**, 855).—Anthraquinonesulphonic acids are converted into the corresponding aminoanthraquinones by heating them with aqueous ammonia in such a manner that the sulphurous acid produced is converted into a practically insoluble metallic salt; for example, the reaction may be carried out in the presence of barium chloride or other soluble barium salt. C. S.

Preparation of Aminoanthraquinones or Their Derivatives. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (Brit. Pat. 8917 of 1914; from *J. Soc. Chem. Ind.*, 1914, **33**, 826).—The carbamides produced by the action of carbonyl chloride on 3-aminobenzophenone-2′-carboxylic acid or its derivatives are converted into the corresponding anthraquinone derivatives by concentrated or fuming sulphuric acid at 80—90°. By heating for a longer period or at a higher temperature, hydrolysis occurs and the corresponding aminoanthraquinones are obtained.

When derivatives of 3-aminobenzophenone-2′-carboxylic acid unsubstituted in position 6 are employed, the corresponding carbamides yield mainly 2-aminoanthraquinonyl derivatives, only a small proportion of the 1-aminoanthraquinonyl derivative being formed.

On the other hand, carbamides substituted in position 6, such as those obtained from 6-halogen-3-aminobenzophenone-2′-carboxylic acids, yield exclusively 1-aminoanthraquinonyl derivatives. C. S.

Preparation of 3-Bromo-2-aminoanthraquinone. W. JUNGHANS (D.R.-P. 273809; from *J. Soc. Chem. Ind.*, 1914, **33**, 783).—3-Bromo-2-aminoanthraquinone is obtained by treatment of 2-aminoanthraquinone with bromine (1 mol.) in the presence of an organic diluent and with or without water. T. H. P.

Preparation of β-Bromoaminoanthraquinones. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 275299; from *J. Soc. Chem. Ind.*, 1914, **33**, 783).—Bromoaminoanthraquinones, in which at least one β-position in the ortho-position to the amino-group is unoccupied, are heated either alone or with sulphuric or phosphoric acid, zinc chloride, etc., at a temperature favourable to the migration of the bromine atom, for example, 160—240°. T. H. P.

Preparation of α-Nitro-derivatives of Acylated Diaminoanthraquinones. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 268984; from *J. Soc. Chem. Ind.*, 1914, **33**, 246).—When an acyl derivative of 1 : 4-diaminoanthraquinone is treated with a nitrating agent in concentrated sulphuric acid solution, the nitro-group enters an α-position in the nucleus not containing the amino-groups. Subsequent elimination of the acyl group yields *5-nitro*-1 : 4-*diaminoanthraquinone*. T. H. P.

Preparation of Condensation Products of the Anthraquinone Series Containing Nitrogen. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 270789; from *J. Soc. Chem. Ind.*, 1914, **33**, 474—475).—Treatment of α-anthraquinonylarylglycines (see succeeding abstract) with acetic anhydride yields yellow compounds which dissolve in alcohol or chloroform and exhibit a marked yellowish-green fluorescence. Their constitution has not been determined. T. H. P.

Preparation of Condensation Products of the Anthraquinone Series Containing Nitrogen. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 270790 and 272613; from *J. Soc. Chem. Ind.*, 1914, **33**, 475, 637).—Anthraquinonyl derivatives of arylglycines of the general formula $NRX{\cdot}CH_2{\cdot}CO_2H$, where R represents the anthraquinonyl nucleus and X an aryl radicle, are obtained by heating α-halogenated anthraquinones or their derivatives or substitution products with salts of aromatic glycine derivatives in presence of (1) copper or its salts and an indifferent solvent or diluent at above 100°, or (2) compounds, such as acetates, which combine with acids, at a high temperature, for instance, 160—170°. T. H. P.

Preparation of Nitrogenous Condensation Products of the Anthraquinone Series. FARBWERKE VORM. MEISTER LUCIUS & BRÜNING (D.R.-P. 272614; from *J. Soc. Chem. Ind.*, 1914, **33**, 638,

Compare A., 1913, i, 1368).—α-Arylaminoanthraquinones, or the acridine compounds derived from them, are fused with naphthols and zinc chloride. T. H. P.

Preparation of 4-Chloro-1-hydroxyanthraquinone and its Derivatives. F. ULLMANN (Brit. Pat. 15058 of 1914; from *J. Soc. Chem. Ind.*, 1914, **33**, 913).—1-Hydroxyanthraquinone or a derivative thereof is treated with sulphuryl chloride in the presence of nitrobenzene or other solvent, with or without the addition of iodine or other catalyst. The chlorine atom enters position 4, 4-chloro-1-hydroxyanthraquinone or a derivative thereof being produced. Polychloroderivatives are obtained by the further action of sulphuryl chloride in the presence of a catalyst. C. S.

Preparation of an Anthraquinone Derivative. R. SCHOLL (D.R.-P. 274784; from *J. Soc. Chem. Ind.*, 1914, **33**, 783).—When alizarin or one of its salts is dissolved in potassium hydroxide solution and treated with a hypochlorite or with chlorine, two alizarin molecules become united with loss of two hydrogen atoms and formation of tetrahydroxydianthraquinonyl. T. H. P.

Preparation of 2-Nitroquinizarin (2-Nitro-1 : 4-dihydroxyanthraquinone). FARBENFABRIKEN VORM. FRIEDRICH BAYER & CO. (Fr. Pat. 461094; Brit. Pat. 17780 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 19).—The treatment of quinizarin with concentrated nitric acid, alone or in the presence of sulphuric acid, results in the formation of nitropurpurin, whilst treatment with nitric acid in the presence of boric acid or other substance which prevents oxidation, produces no nitration. On the other hand, *2-nitroquinizarin* is easily obtained by the action of nitric acid on quinizarin in the presence of an inert solvent or diluent, such as glacial acetic acid or nitrobenzene. The product consists of brick-red crystals, and dissolves in sulphuric acid to a cerise-red, non-fluorescent solution. Wool with an alum mordant is dyed claret to brown, and with a chromium mordant violet-brown to brown. C. S.

Preparation of Anthraquinone Derivatives. R. SCHOLL (D.R.-P. 274783; from *J. Soc. Chem. Ind.*, 1914, **33**, 783).—When dianthraquinonyl derivatives, containing in each anthraquinone nucleus at least one hydroxyl group in an ortho-position to the dianthraquinonyl linking, are heated at high temperatures either alone or in the presence of a condensing agent, one molecule of water is eliminated, with formation of a furan derivative. T. H. P.

Chlorinated Derivatives of 2-Methylanthraquinone. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (Fr. Pat. 460432; from *J. Soc. Chem. Ind.*, 1914, **33**, 18).—It is known that 2-methylanthraquinone is converted into chloromethyl derivatives by heating with chlorine under pressure. It has now been found that chloromethylanthraquinones containing the chlorine in the anthraquinonyl nucleus are obtained by treating 2-methylanthraquinone or a derivative with

chlorine or its equivalent in the presence of a catalyst such as iodine. For example, 1-chloro-2-methylanthraquinone is obtained by heating on the water-bath under a reflux condenser a mixture of 15 parts of 2-methylanthraquinone, 25 parts of nitrobenzene, 1 part of iodine, and 15—20 parts of sulphuryl chloride; the reaction is complete in eight to ten hours, and the product is separated by crystallisation and the addition of alcohol. C. S.

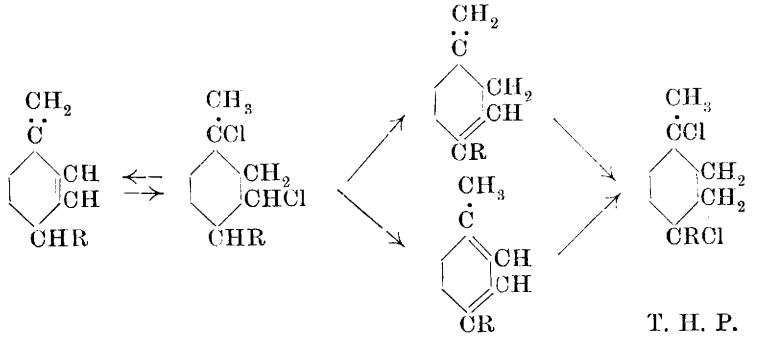
Synthesis of a Benzoylated Alkylamine of the Camphor Group. ANTONIO MADINAVEITIA (*Anal. Fis. Quim.*, 1914, **12**, 428—432).—The hydrochloride of benzoyl-α-dimethylaminoethylborneol has been synthesised by the action of magnesium ethyl bromide on α-dimethylaminocamphor, followed by benzoylation of the hydroxyl group of the corresponding tertiary alcohol. *α-Dimethylaminoethylborneol* is an oil, b. p. 134—135°. *Benzoyl-α-dimethylaminoethylborneol hydrochloride* is a crystalline solid. A. J. W.

Preparation of Therapeutically-Active Esters of the Terpene Series. KALLE & Co. (D.R.-P. 273850; from *J. Soc. Chem. Ind.*, 1914, **33**, 806).—When bromo-derivatives of alkyl- or aryl-acetic acids of the general formula $CRR'Br\cdot CO_2H$, where R and R′ represent alkyl or aryl radicles, are condensed in the usual manner with terpenic alcohol, the resulting esters possess soporific properties resembling those of the bromodialkylacetamides. T. H. P.

Action of Alcoholic Hydrogen Chloride on β-Phellandrene and the Mechanism of the Transformation of the Terpenes by means of Acids. L. FRANCESCONI and E. SERNAGIOTTO (*Gazzetta*, 1914, **44**, ii, 456—462).—When treated in the cold with alcoholic hydrogen chloride, β-phellandrene yields an oily hydrochloride, together with α-terpinene dihydrochloride. α-Terpinene is the only terpene stable to the isomerising action of mineral acids, and is the point at which all mono- and bi-cyclic terpenes arrive on the insertion of lateral chains in the para-position of the hexamethylene nucleus; it is also the only terpene containing in the nucleus two conjugated double linkings with two tertiary carbon atoms.

As regards their conversion into α-terpinene or its hydrochloride, the terpenes are divided into three groups, according as the transformation takes place: (1) by direct saturation of the double linkings or by rupture of the ring, the halogen combining with the least highly hydrogenated carbon atom: α- and β-terpinolene, β-terpinene and sabinene; (2) by way of dipentene, and therefore with previous migration of the double linkings: dipentene, limonene and β-pinene; (3) by migration of the double linkings in a manner different from case (2): phellandrene.

The transformation of β-phellandrene into α-terpinene dihydrochloride is regarded as taking place in accordance with the scheme:



T. H. P.

Essential Oil of Helichrysum saxatile (Moris). L. Francesconi and E. Sernagiotto (*Gazzetta*, 1914, **44**, ii, 419–421).—*Helichrysum saxatile*, found in various parts of Sardinia, yields a yellow essential oil, having a pungent but pleasant odour, which, especially when highly diluted, recalls that of the rose; D 0·9020, n_D 1·4769, $[\alpha]_D$ −11·71° in 13% alcoholic solution. It does not give Schiff's reaction or reduce ammoniacal silver nitrate solution. It is free from acids, phenols and pinene or other normal terpenes. It distils mostly at 240°, leaving no residue of paraffin. The distillate contains C 79·50% and H 12·11%, but its individuality has not been established. The optical activity and the physical properties of the oil render probable the presence of a compound belonging to the hydroaromatic series, possibly an oxygenated sesquiterpene derivative. T. H. P.

Volatile Oils of the Genus Solidago. Emerson R. Miller and Milner H. Eskew (*J. Amer. Chem. Soc.*, 1914, **36**, 2538—2541).—The composition of the volatile oil of *Solidago canadensis* has been studied by Schimmel & Co. (Report, April, 1894, 57), but the oils of the other species of *Solidago* have not hitherto been investigated. An account is now given of the volatile oil of *S. nemoralis*.

On distillation with steam, the fresh herb (root excluded), collected in the flowering stage, yielded, on the average, 0·322% of volatile oil which was olive-green, had a peculiar odour, and gave the following constants: D_{25}^{25} 0·8532; α_D −16·17°; n_D^{18} 1·47397; saponification number, 5·6; saponification number after acetylation, 9·4; it was soluble in about 4 volumes of 90% alcohol, or in 24 volumes of 70% alcohol. The oil consists chiefly of *d*- and *l*-α-pinene, and also contains acetic and salicylic acids, an alcohol and its acetate, and probably borneol.

E. G.

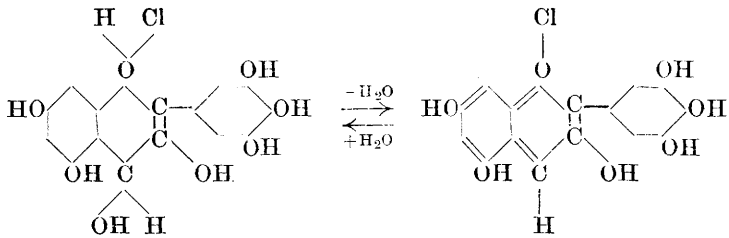
Presence of Nopinene in Spanish Oil of Turpentine. B. Dorronsoro and O. Fernández (*Anal. Fis. Quim.*, 1914, **12**, 424—426).—A reply to Madinaveitia (A., 1914, i, 1171). The sample of oil of turpentine investigated by the authors was derived from *Pinus Halepensis*. The absence of nopinene is proved by the non-production of a nopate on oxidation with alkaline permanganate, and confirmed by the fact that its b. p. is 154—155° and its rotation +1°. Nopinene is lævorotatory, and has b. p. 163°. A. J. W.

Preparation of Saline Double Compounds from Cantharidylethylenediamine. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 272291; from *J. Soc. Chem. Ind.*, 1914, **33**, 568).—Treatment of the base obtained by the condensation of cantharidin and ethylenediamine with salts of the heavy metals other than gold (compare A., 1914, i, 708) yields products of medicinal value. T. H. P.

Production of Anthocyanins and Anthocyanidins. II. ARTHUR ERNEST EVEREST (*Proc. Roy. Soc.*, 1914, [*B*], **88**, 326—332. Compare A., 1914, i, 978).—The red pigments obtained by the author by the gentle reduction of yellow flavonol derivatives have been compared with natural cyanin. The similarity in the behaviour of the pigments confirms the author's conclusion that the reduction products are true anthocyanins and anthocyanidins (compare Willstätter, A., 1914, i, 564).

The artificial anthocyanins resemble the natural anthocyanins in the following particulars: (1) stability in acid solution—aqueous or alcoholic; (2) absorption spectrum, consisting of a single broad band which becomes flatter towards the violet, and extends over a great portion of the green and blue regions; (3) oxidation in acid solution, forming colourless products; (4) loss of colour on reduction, with restoration of colour on the addition of hydrogen peroxide; (5) formation of violet or reddish-violet compounds in neutral solutions (obtained by shaking with excess of calcium carbonate), giving red compounds with acids (oxonium salts), and blue or bluish-green compounds with alkalis; (6) instability in the presence of alkalis; (7) decoloration in neutral solutions, due to isomerisation, and quantitative return of colour on treatment with an acid.

The last point of similarity has been explained by the author by the scheme



Colourless product. Anthocyan pigment from myriectin.

and this has received confirmation by the work of Willstätter and Mallison (A., 1914, i, 1081).

Rutin (a glucosidic pigment consisting of quercetin combined with a disaccharose residue and identical with viola-quercitrin) gives on reduction a red anthocyanin which may be identical with cyanin. On hydrolysis, the corresponding anthocyanidin is obtained, which behaves exactly as cyanidin. The identity has, however, not yet been conclusively proved. H. W. B.

A Supposed Synthesis of Anthocyanin. M. WHELDALE and H. LL. BASSETT (*J. Genetics*, 1914, **4**, 103—107); ARTHUR ERNEST EVEREST (*ibid.*, **4**, 191—192).—Polemical.

Modern Dyes and Dyeing. GILBERT T. MORGAN (*Econ. Proc. Roy. Dublin Soc.*, 1914, **2**, 123—141).—A lecture delivered before the Royal Dublin Society. W. G.

Preparation of Coumarin. KINZLBERGER & Co. (D.R.-P. 276667; from *J. Soc. Chem. Ind.*, 1914, **33**, 1036).—Chloro-β-phenylpropionic acid is heated with an alkali hydroxide at above 200° under pressure and the melilotic acid, thus produced in good yield, converted by heating into hydrocoumarin, which is dehydrogenated, for instance, by heating with chlorine or sulphur, at a temperature near the boiling point of coumarin. T. H. P.

Preparation of Hydrogenised Organic Substances or Compounds [of the Opium Group]. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (Brit. Pat., 14247 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 844).—Morphine, codeine, and other opium compounds are hydrogenised by treating them with formic acid and a finely divided metal of the platinum group, or a colloidal solution of such metal. For example, 5 parts of codeine hydrochloride are dissolved in 70 parts of a 1% solution of formic acid and mixed with the palladium black obtained from 0·5 part of palladous chloride. The mixture is kept at the ordinary temperature for a few hours and then at 50° until the evolution of carbon dioxide ceases. The solution is filtered, treated with an excess of sodium hydroxide, saturated with sodium chloride, and extracted with ether. The extract contains the hydrocodeine, which can be crystallised from water. C. S.

Preparation of 2 : 6-Diphenyl-1-methyl-4-piperidone. J. D. RIEDEL (D.R.-P. 269429; from *J. Soc. Chem. Ind.*, 1914, **33**, 278).—This compound, obtained by condensation of distyryl ketone and methylamine, finds therapeutic application. T. H. P.

Preparation of Pyridinecarboxylic Acids and of Pyridine. A. HEINEMANN (Brit. Pat. 17003 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 889).—Homologues of pyridine, phenylpyridines, and quinolines can readily be oxidised to pyridinecarboxylic acids by ozone, ozonised oxygen, or ozonised air at the ordinary temperature. The ozone can be passed into a vessel containing the pyridine derivative, or it can be generated at the anode of an electrolytic cell, in which the pyridine derivative is oxidised; in the latter case, it is advisable to surround the cathode by diaphragms to prevent reduction of the carboxylic acids. When it is desired to prepare pyridine, the carboxylic acid is distilled, and, if necessary, the process of oxidation is repeated until the product consists of pure pyridine. C. S.

Process of Preparing Reduction Products of Phthalimide. KALLE & Co. (D.R.-P. 267596; from *J. Soc. Chem. Ind.*, 1914, **33**, 193).—When phthalimide is reduced at the ordinary temperature by means of zinc dust and alkali hydroxide solution, hydroxyphthalimidine, $C_6H_4<\begin{matrix}CH(OH)\\CO\end{matrix}>NH$, is formed, whilst in the hot the same reaction

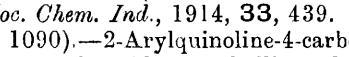
leads to the replacement of the imino-group by oxygen and of the hydroxyl group by hydrogen, phthalide being produced. T. H. P.

Preparation of Esters of 2-Alkyl- or 2-Aryl-quinoline-carboxylic Acids or their Derivatives. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 275963; from *J. Soc. Chem. Ind.*, 1914, **33**, 943).—A soluble salt of a 2-alkyl- or 2-aryl-quinoline-carboxylic acid or derivative thereof, whether substituted in the benzene or in the pyridine ring, is esterified by treatment with an alkyl haloid in presence of water at a high temperature. T. H. P.

2-Arylquinoline-4-carboxylic Acids. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (Brit. Pat. 11836 of 1914; from *J. Soc. Chem. Ind.*, 1914, **33**, 889).—Largely increased yields of 2-aryl-quinoline-4-carboxylic acids are obtained by adding less than one mol. of pyruvic acid to a boiling alcoholic solution of benzylideneaniline (1 mol.) or other condensation product of an aromatic amine and an aromatic aldehyde. Usually the best results are obtained when about 3 mol. of pyruvic acid and 4 mol. of benzylideneaniline are employed. The solution of pyruvic acid is preferably added at 0—5°, and it is not necessary to use the pure acid. Further, the process can be carried out without decreasing the yield, if dilute alcohol is used as the solvent; in this case, 2-phenylquinoline-4-carboxylic acid, for example, crystallises quantitatively from the solution on cooling. The yields obtained correspond with about 180—185% of the pyruvic acid used, when benzylideneaniline is employed. C. S.

Preparation of 2-Arylquinoline-4-carboxylic Acids. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (Brit. Pat. 15481 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 439. Compare A., 1913, i, 92; 1914, i, 992, 1090).—2-Arylquinoline-4-carboxylic acids can be prepared by adding pyruvic acid to a boiling alcoholic solution of a derivative or homologue of aniline and benzaldehyde, piperonal, vanillin, or other suitable aromatic aldehyde. Thus *p*-toluidine, benzaldehyde, and pyruvic acid yield 2-phenyl-6-methylquinoline-4-carboxylic acid. The use of benzidine or its homologues in a similar manner gives rise to the corresponding diquinolyl derivatives.

2-*β*-*Hydroxy*-m-*methoxyphenyl*-6-*methylquinoline*-4-*carboxylic acid*,



m. p. 217—219°, is obtained from *p*-toluidine, vanillin, and pyruvic acid. C. S.

Preparation of Quinoline Compounds. ELI LILLY & Co. (U.S. Pat. 1098022; from *J. Soc. Chem. Ind.*, 1914, **33**, 844).—Equal molecular quantities of salicylaldehyde, pyruvic acid, and a suitable aromatic amine, for example, *p*-toluidine, are boiled in absolute alcoholic solution; the product is allowed to crystallise. 2-*o*-Hydroxyphenyl-6-methylquinoline-4-carboxylic acid is produced when the amine is *p*-toluidine. C. S.

Preparation of 6-Hydroxy-2-piperonylquinoline-4-carboxylic Acid. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (Brit. Pat. 15482 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 766).—An alcoholic solution of *p*-aminophenol is boiled with an alcoholic solution of piperonal and pyruvic acid. The precipitated 6-hydroxy-2-piperonylquinoline-4-carboxylic acid is purified through its sodium salt. C. S.

Preparation of α-Arylamides of β-Naphthisatin. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (Brit. Pat. 30072 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 246. Compare C. and H. Dreyfus, A., 1904, i, 832, 893).—Hydrocyanocarbodi-β-naphthylimide or mixed hydrocyanocarbo-β-naphthylarylimides can be converted into α-arylamides of β-naphthisatin by treatment with aluminium chloride in the absence of water. Intermediate products containing aluminium are formed during the reaction, but they can be easily converted into the free arylamides, for example, by treatment with cold concentrated hydrochloric acid. C. S.

Preparation of Nitration Products of Dihalogenated Carbazoles. G. LIST (D.R.-P. 275833; from *J. Soc. Chem. Ind.*, 1914, **33**, 826).—Carbazole is treated with a halogen or its equivalent in glacial acetic acid solution and at the end of the reaction the product is treated with concentrated nitric acid. The dihalogenated nitrocarbazoles thus produced differ from those known in the possession of at least one labile halogen atom; the reactivity of the halogens may be increased by the introduction of a sulphonic or other acidic group into the molecule. T. H. P.

Preparation of Triaminocarbazolesulphonic Acid. L. CASSELLA & Co. (D.R.-P. 275975; from *J. Soc. Chem. Ind.*, 1914, **33**, 854).—When carbazole is highly sulphonated, preferably until a trisulphonic acid is formed, and this treated with powerful nitrating agents, not only are the sulphonic groups replaced by nitro-groups, but a furthur nitro-group is introduced. The trinitrocarbazolesulphonic acid thus obtained may be reduced to triaminocarbazolesulphonic acid. T. H. P.

Preparation of Anthraquinone-*N*-1 : 1′-oxazine. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 273444; from *J. Soc. Chem. Ind.*, 1914, **33**, 638. Compare A., 1914, i, 203).—Anthraquinone-*N*-1 : 1′-oxazine is obtained by the action of condensing agents on the 2-methoxy-1 : 1′-dianthrimide formed by the interaction of 1-chloroanthraquinone and 1-amino-2-methoxyanthraquinone. T. H. P.

Preparation of *o*-Aminophenylsulphonylacetic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 269337; from *J. Soc. Chem. Ind.*, 1914, **33**, 277).—*o*-Nitrophenylsulphonylacetic acid is reduced by means of zinc dust or iron in neutral or feebly acid (organic) solution, the mixture being then rendered alkaline and the free *o*-aminophenylsulphonylacetic acid separated from the filtered solution of its alkali salt by addition of the equivalent proportion of an acid in the cold. The acid may be readily converted into sulphazone (see succeeding abstract). T. H. P.

Preparation of Sulphazone. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 269428 ; from *J. Soc. Chem. Ind.*, 1914, **33**, 278).—Sulphazone is obtained in about 95% yield by treatment of *o*-nitrophenylsulphonylacetic acid with iron in neutral solution or suspension, preferably in presence of a neutral salt, and subsequent addition of excess of a mineral acid. Claasz's process (D.R.-P. 256342) gives a yield of about 77%. T. H. P.

Preparation of Naphthalenesulphonic Derivatives of Aromatic *p*-Diamines. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 271821 ; from *J. Soc. Chem. Ind.*, 1914, **33**, 544).—Condensation of an aromatic *p*-diamine with an aminonaphthalenesulphonic acid, with or without addition of a solvent or suspending agent, appears to yield principally monosubstituted compounds of the type

$$NH_2 \cdot R \cdot NH \cdot C_{10}H_6 \cdot SO_3H,$$

which form valuable components of azo-colouring matters ; the dinaphthalenesulphonic derivatives are produced only in small proportion. T. H. P.

Preparation of 4:4′-Diaminodibenzyl Sulphide and its Derivatives. CHEMISCHE FABRIK VORM. WEILER-TER-MEER (D.R.-P. 272292 ; from *J. Soc. Chem. Ind.*, 1914, **33**, 637).—Aromatic amines or their homologues or substitution products, such as aniline, ethylaniline, *o*- or *m*-toluidine, *o*-chloroaniline, metanilic acid, *m*-phenylenediamine or α-naphthylamine, in which the para-position to the amino-group or groups is unoccupied, are treated with formaldehyde and an alkali thiosulphate in presence of an acid. The products obtained are derivatives of 4 : 4′-diaminodibenzyl sulphide, $(NH_2 \cdot C_6H_4 \cdot CH_2)_2S$. T. H. P.

Preparation of 5(4)-Methyl-4(5)-arylaminomethylglyoxalines. O. GERNGROSS (D.R.-P. 276541 ; from *J. Soc. Chem. Ind.*, 1914, **33**, 1004).—Treatment with an alkaline reducing agent of the Schiff's bases obtained by condensing 5(4)-methyliminazyl-4(5)-glyoxylic acid with a primary aromatic amine of the benzene series yields compounds of the constitution $\begin{matrix} CH{=}{=}N \\ | \\ NH \cdot CMe \end{matrix}\!\!>\!C \cdot CH_2 \cdot NHX$, where X is an aryl radicle. T. H. P.

Carbamides of *peri*Naphthindantrione. E. CALDERARO (*Gazzetta*, 1914, **44**, ii, 389—394).—The compound obtained by Errera and Sorgés (A., 1914, i, 59) by the condensation of *peri*naphthindantrione with carbamide has neither of the formulæ suggested by these authors, but is a carbamide of the structure

$$C_{10}H_6\!<\!\begin{matrix} CO \\ CO \end{matrix}\!>\!C\!<\!\begin{matrix} NH \\ NH \end{matrix}\!>\!CO,$$

and is analogous to those prepared by Grimaldi (A., 1897, i, 575) from anthraquinone, phenanthraquinone and *p*-benzoquinone, and by Ampola and Recchi (A., 1899, i, 918) from acenaphthenequinone. This conclusion is based on the observations that *peri*naphthindantrione con-

denses only with those substituted carbamides in which each of the nitrogen atoms retains at least one atom of hydrogen, and that ethylurethane, containing only one amino-group, behaves in a totally different manner. Of the three carbonyl groups of the triketone, that reacting with carbamides is most probably the middle one, since the resulting carbamides do not condense with *o*-phenylenediamine.

peri*Naphthindantrionemonocarbamidephenylhydrazone*,

$$C_{10}H_6\langle\begin{matrix}C(:N_2HPh)\\ \text{---}CO\text{---}\end{matrix}\rangle C\langle\begin{matrix}NH\\ NH\end{matrix}\rangle CO,$$

forms shining, yellow leaflets, decomposing and blackening at 300°.

peri*Naphthindantrionemethylcarbamide*,

$$C_{10}H_6\langle\begin{matrix}CO\\ CO\end{matrix}\rangle C\langle\begin{matrix}NMe\\ NH\text{---}\end{matrix}\rangle CO,$$

obtained from the triketone and methylcarbamide, forms an almost colourless, crystalline crust, remaining unchanged at 325°. Its *phenylhydrazone*, $C_{21}H_{16}O_2N_4$, forms minute, yellow needles, decomposing and blackening at about 300°.

peri*Naphthindantrione-ethylcarbamide*, $C_{16}H_{12}O_3N_2$, forms a colourless, crystalline crust, m. p. 286—287°.

peri*Naphthindantrionephenylcarbamide*, $C_{20}H_{12}O_3N_2$, forms a white, crystalline powder, m. p. 266—267°.

peri*Naphthindantrionedimethylcarbamide*,

$$C_{10}H_6\langle\begin{matrix}CO\\ CO\end{matrix}\rangle C\langle\begin{matrix}NMe\\ NMe\end{matrix}\rangle CO,$$

prepared from *s*-dimethylcarbamide, forms a colourless, crystalline crust, m. p. 179—180°.

peri*Naphthindantrionediethylcarbamide*, $C_{18}H_{16}O_3N_2$, forms a colourless, crystalline crust, m. p. 151—152°, and, like the preceding compound, yields a yellow liquid on fusion.

The condensation of *peri*naphthindantrione with ethylurethane yields the compound

$C_{10}H_6\langle\begin{matrix}CO\\ CO\end{matrix}\rangle C(OH)\cdot NH\cdot CO_2Et$, or, more probably,

$$C_{10}H_6\langle\begin{matrix}CO\\ CO\end{matrix}\rangle C(OEt)\cdot O\cdot CO\cdot N\dot{H}_2,$$

which forms hard, yellowish-brown crystals, m. p. 140° (decomp.), resolidifying at the same temperature to a red mass; its thermal decomposition yields cyanuric acid and *peri*naphthindantrione hydrate.

T. H. P.

Preparation of Compounds and Colouring Matters of the Anthraquinone Series. Badische Anilin- & Soda-Fabrik (Brit. Pat. 21027 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 544). —Vat dyes producing generally lemon-yellow shades and having probably the constitution $A\langle\begin{matrix}N\\ S\text{-}\end{matrix}\rangle C\cdot C\langle\begin{matrix}N\\ S\text{-}\end{matrix}\rangle A$ or

$$A\langle\begin{matrix}NH\\ S\text{-}\end{matrix}\rangle C{:}C\langle\begin{matrix}NH\\ S\text{-}\end{matrix}\rangle A$$

(where A represents the anthraquinone nucleus), are produced by treating an *o*-halogenacetylaminoanthraquinone with sulphur or a sub-

stance capable of yielding sulphur, or alternatively by treating an *o*-aminoanthraquinonyl mercaptan with a compound capable of yielding an oxalyl group, for example, oxalyl chloride. C. S.

Preparation of Triazoles of the Aromatic Series. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (Brit. Pat. 29224 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 247).—*o*-Aminoazo-dyes of the benzene, naphthalene, or anthracene series can be converted easily, and with good yields, into the corresponding triazoles by heating with metals acting as catalysts, in the presence of organic solvents of high b. p.

Benzeneazo-β-naphthylamine (100 parts) and finely divided copper (1 part) are heated for five hours in boiling nitrobenzene (1000 parts); 2-phenylnaphthatriazole is isolated by filtering the solution and expelling the solvent by distillation with steam. C. S.

The Curdling (Coagulation) of Milk and the Solubility of the Curd in Sodium Chloride Solution. ORLA-JENSEN, BETZY MEYER and ANNA D. ORLA-JENSEN (*Oversigt K. Danske Vidensk. Selsk. Forh.*, 1914, 287—309).—Experiments on the precipitation by calcium chloride of solutions of the various sodium and calcium salts of caseinogen lead the authors to the conclusion that when the caseinogen is first precipitated by calcium chloride from milk at high temperatures (80°), the precipitation is due rather to the calcium citrate and other salts contained in the milk than to the added calcium chloride.

The fission of caseinogen into paracasein and whey-albumin, which the authors consider takes place when milk is curdled with rennet, is not accompanied by an increase in the Sørensen formalin titre.

The curdling of milk by acids begins at 35° before all the calcium has been displaced from the calcium caseinogenate. Equivalent quantities of different acids are necessary to curdle equal quantities of the same milk at a given temperature, but the acids act at different rates. The so-called "acid-curdling" of weakly acid milk at high temperatures is due more to the calcium salts present than to the acid; the precipitating action of the calcium ion on the caseinogen increases with rise in temperature, and the acid changes the dicalcium into the monocalcium caseinogenate, which is much more readily precipitated.

Calcium caseinogenate and caseinate give clear solutions with sodium chloride, since they are changed into the sodium salts. A solution of dicalcium caseinogenate containing sodium chloride is much more readily precipitated by calcium chloride than a similar solution of monocalcium caseinogenate. In the case of milk, the calcium salts present (citrate, phosphate, etc.) tend to prevent the transformation of the calcium caseinogenate into the sodium salt and the milk does not become translucent until sufficient acid has been added to transform the dicalcium into the monocalcium caseinogenate, which then goes into solution. T. S. P.

Action of Rennin on Caseinogen. ALFRED W. BOSWORTH (*J. Biol. Chem.*, 1914, **19**, 397—398. Compare A., 1913, i, 1116).—The similarity between the results of the analyses of caseinogen and of

casein prepared from caseinogen by the action of rennin and of trypsin is advanced by the author as conclusive evidence in favour of the view that the transformation of caseinogen into casein is a hydrolytic process, one molecule of caseinogen yielding two molecules of casein, and that this hydrolysis of caseinogen is not accompanied by a cleavage of any of the elements contained in the original caseinogen molecule (compare Harden and Macallum, A., 1914, i, 442).

H. W. B.

Preparation of Nitro- and Dinitro-aminophenylarsinic Acids or Substitution Derivatives Thereof Substituted in the Amino-group. C. F. Boehringer & Söhne (Brit. Pat. 29546 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 806).—Compounds are formed by the interaction of ammonia or substituted ammonias and 4-chloro-3-nitrophenylarsinic acid or 4-chloro-3 : 5-dinitrophenylarsinic acid. The compounds obtained from 4-chloro-3-nitrophenylarsinic acid can be further nitrated. C. S.

Preparation of Derivatives of Trinitromethylaminophenylarsinic Acid. C. F. Boehringer & Söhne (U.S. Pat. 1081079; Brit. Pat. 9969 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 41).—By treatment with a reducing agent such as tin and hydrochloric acid, ω : 3 : 5-trinitro-4-methylaminophenylarsinic acid is converted into 3 : 5 : 3′ : 5′-*tetra-amino*-4 : 4′-*dimethylaminoarsenobenzene*, m. p. about 95° (decomp.). C. S.

Preparation of a Dihydroxyphenylarsinic Acid. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 271892; from *J. Soc. Chem. Ind.*, 1914, **33**, 567—568).—The treatment of 4-hydroxyphenyl arsinic acid with potassium persulphate in aqueous alkali solution results in the introduction of a second hydroxyl group into the benzene nucleus, with formation of a dihydroxyphenylarsinic acid.

T. H. P.

Preparation of 3 : 5-Dihydroxyphenylarsinic Acid. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 272690; from *J. Soc. Chem. Ind.*, 1914, **33**, 667).—3 : 5-Dihydroxyphenylarsinic acid is obtained by heating resorcinol with arsenic acid. T. H. P.

Preparation of Phenylmethylglycine-*p*-arsinic Acid and of its Reduction Product, Arsenobenzene-*pp*′-dimethylaminoacetic Acid. Les Etablissements Poulenc frères and K. Oechslin (Fr. Pat. 462276; from *J. Soc. Chem Ind.*, 1914, **33**, 276).—The esters of phenylmethylglycine-*p*-arsinic acid, obtained by the action of arsenic trichloride on phenylmethylglycine esters, are very easily hydrolysed by an excess of sodium hydroxide at about 60°; by acidifying with acetic or hydrochloric acid, *phenylmethylglycine*-p-*arsinic acid* is precipitated in the form of colourless crystals. It is sparingly soluble in water, and when heated does not melt but evolves carbon dioxide with the formation of *p*-dimethylaminophenylarsinic acid.

The reduction of phenylmethylglycine-*p*-arsinic acid by sodium hyposulphite at a high temperature results in the formation of *arsenobenzene-*

pp'-*dimethylaminoacetic acid*, which is stable towards air and oxidising agents, and dissolves in solutions of sodium hydroxide or carbonate, forming neutral salts. C. S.

Preparation of Hexa-aminoarsenobenzene, Triaminophenylarsinic Acid, and Tetranitrodiaminoarsenobenzene. C. F. BOEHRINGER & SÖHNE (Brit. Pat. 7488 and 8137 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 41, 438).—I. 3:5-Dinitro-4-aminophenylarsinic acid is reduced to 3:4:5:3':4':5'-hexa-aminoarsenobenzene by acid reducing agents, such as tin or stannous chloride and hydrochloric acid. The free base is very unstable, rapidly darkens in air, and is insoluble in the usual organic solvents, but dissolves in dilute acids. It is stated to have a very powerful spirillocide effect, with comparatively small toxicity.

II. The preceding reduction can be effected in two or more stages. The first stage can be effected by sodium hyposulphite, whereby 3:4:5-triaminophenylarsinic acid is produced; this can be further reduced to 3:4:5:3':4':5'-hexa-aminoarsenobenzene by hypophosphorous acid. Again, treatment of 3:5-dinitro-4-aminophenylarsinic acid by 50% phosphorous acid at about 40° in the presence of alcohol results in the production of a tetranitrodiaminoarsenobenzene, which can be converted into the hexa-aminoarsenobenzene by stannous chloride and hydrochloric acid. C. S.

Preparation of Alkali Salts of Diaminodihydroxyarsenobenzene in Combination with Copper and Silver. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (Brit. Pat. 1247 of 1914; from *J. Soc. Chem. Ind.*, 1914, **33**, 942).—A solution of 3:3'-diamino-4:4'-dihydroxyarsenobenzene is mixed with small quantities of a silver or copper salt, sodium hydroxide is added, and the compound formed is isolated by precipitation or by evaporating the solution. It is of great value for the treatment of sleeping sickness. C. S.

Preparation of Neutral Derivatives of 3:3'-Diamino-4:4'-dihydroxyarsenobenzene, Soluble in Water. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 271893; from *J. Soc. Chem. Ind.*, 1914, **33**, 568).—3:3'-Dinitro-4:4'-dihydroxyarsenobenzene is used in place of the corresponding diamino-compound or of the 3-nitro- or 3-amino-4-hydroxyphenyl-1-arsinic acid formerly employed (compare A., 1913, i, 116, 1121). T. H. P.

Preparation of 3:3'-Diamino-4:4'-dihydroxyarsenobenzene. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 271894; from *J. Soc. Chem. Ind.*, 1914, **33**, 568).—3-Nitro-4-hydroxyphenylarsinic acid or 3:3'-dinitro-4:4'-dihydroxyarsenobenzene or 3-nitro-4-hydroxyphenylarsenious oxide is reduced by means of hypophosphorous acid or of phosphorous acid and potassium iodide or hydriodic acid, preferably in presence of acetic acid (compare A., 1914, i, 761). T. H. P.

Preparation of Arsenic-Antimony Compounds. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (U.S. Pat. 1111821; from *J. Soc. Chem. Ind.*, 1914, **33**, 1075).—Organic arsenic-antimony compounds

are obtained by treating with a strong reducing agent a mixture of an aromatic arsinic acid and an antimony compound in solution. The products are insoluble in water, but dissolve in dilute hydrochloric acid or dilute sodium hydroxide. C. S.

Preparation of Organic Mercury Compounds. E. SCHOSSBERGER and G. FRIEDRICH (D.R.-P. 275932; from *J. Soc. Chem. Ind.*, 1914, **33**, 890).—Free terpenic keto-carboxylic acids or their esters react quantitatively with mercury salts, forming stable compounds, which are soluble in alkali solutions, do not lose mercuric oxide when heated, and find medicinal application. The compound from camphor-carboxylic acid and mercuric acetate contains about 44% of mercury. T. H. P.

Preparation of Aromatic Mercury Compounds. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 272289, and Brit. Pat. 2314 of 1914; from *J. Soc. Chem. Ind.*, 1914, **33**, 568).—When aromatic arsenic compounds containing tervalent arsenic are treated with mercuric oxide or a mercuric salt in acid, neutral or alkaline solution, the mercury replaces the arsenic, which separates as arsenious acid, the mercury becoming attached to the benzene nucleus to form compounds of the type HgArX or $HgAr_2$. T. H. P.

Physiological Chemistry.

Effect of Inhalation of Alcohol on the Viscosity of the Blood. R. BURTON-OPITZ (*Amer. J. Physiol.*, 1914, **35**, 265—267. Compare A., 1905, ii, 98).—The inhalation by dogs of air charged with methyl or ethyl alcohol is associated with a marked increase in the viscosity of the blood. The general appearance of the blood, as well as the decided increase in its specific gravity, indicates that the change in the viscosity is due to an accumulation of excretory material rather than to a direct destructive action of the alcohol on the cellular constituents of the blood. The action of methyl alcohol is as great as that of ethyl alcohol, and the changes, in both cases, result very soon after the beginning of the inhalation.

H. W. B.

Changes in the Hydrogen Ion Concentration of the Blood Produced by Pulmonary Ventilation. T. H. MILROY (*Quart. J. expt. Physiol.*, 1914, **8**, 141—154).—Pulmonary ventilation with air, or with air and oxygen, produces a rapid fall in the hydrogen ion concentration of the blood, especially if the period of ventilation is short. This results in apnœa, during which the hydrogen ion concentration rises. Subsequent ventilation with air rich in carbon dioxide raises the hydrogen ion concentration, and no

cessation of breathing takes place. The hydrogen ion concentration is closely related to carbonic acid concentration, and influences the activity of the respiratory centre. W. D. H.

Blood and Urinary Amylase. C. E. KING (*Amer. J. Physiol.*, 1914, **35**, 301—332).—The amylolytic power of the blood and urine of the dog, cat, pig, rabbit, woodchuck, raccoon, goat, opossum, and man, under various conditions, has been estimated by a modification of Wohlgemuth's method (A., 1908, ii, 444).

The amylolytic power of the blood-serum and urine of different species of animals varies in a manner that is not accounted for by differences in diet and feeding habits. The serum of the goat, which is entirely herbivorous, has only about one-twelfth of the amylolytic activity of that of either the dog or the cat. Those animals which secrete an amylolytic enzyme in the saliva have generally, as compared with those the salivary secretion of which is inactive, a larger proportion of amylase in the urine. Feeding with a high carbohydrate diet does not increase the quantity of urinary amylase.

At birth, the pancreas in the case of the dog or cat contains only a little amylase, and the urinary amylase is also low. As the animal grows, the increase in pancreatic amylase is found to run parallel with the output of urinary amylase. Removal of the pancreas leads to an almost complete disappearance of amylase from the urine, and diseases of the pancreas which depress its activity are also associated with a decrease in urinary amylase.

These considerations, and the fact that amylase injected into the blood reappears in the urine, lead the author to the conclusion that urinary amylase arises chiefly by the passage of the amylolytic enzymes from the salivary gland and the pancreas into the blood, and their subsequent elimination by the kidneys. H. W. B.

Prothrombin. W. H. HOWELL (*Amer. J. Physiol.*, 1914, **35**, 474—482. Compare A., 1912, ii, 1078).—The author brings forward evidence in support of the view that the failure of blood to clot in the blood vessels is due to the presence of antithrombin and not to the absence of thrombokinase. Prothrombin is prepared free from all the other constituents of the blood which take part in blood coagulation, with the possible exception of traces of antithrombin, by precipitating oxalated plasma with acetone, and then extracting the dried precipitate with water. The solutions of prothrombin so obtained are fairly stable, and can be heated at 60° without entirely losing their coagulating power. The addition of calcium salts is found to be sufficient to enable this prothrombin to transform fibrinogen into fibrin, the addition of kinase being unnecessary. The objection that the prothrombin is accompanied by kinase has been ruled out by testing with peptone plasma, which is coagulated by kinase, but not by thrombin. The prothrombin extract did not coagulate peptone plasma.

An extract of blood platelets is said to contain both prothrombin

and thromboplastin (the substance which neutralises the action of antithrombin), because of its clotting action on peptone plasma.

The presence of prothrombin in the circulating blood is indicated by the clotting which follows the addition of calcium salts and tissue extract to centrifugalised oxalated plasma. In shed blood, disintegration of the platelets furnishes an additional supply of prothrombin and thromboplastin, both of which are factors tending to hasten the coagulation of the blood. H. W. B.

Coagulation of Lymph. W. H. Howell (*Amer. J. Physiol.*, 1914, **35**, 483—491. Compare preceding abstract).—Lymph plasma contains antithrombin in the same concentration as in blood plasma. When freed from corpuscles by long centrifugalisation, the lymph plasma clots with great slowness, owing to a relative excess of antithrombin. Addition of tissue extract or of kephalin solution to such plasmata causes prompt clotting. The presence of antithrombin in the lymph prevents the activation by calcium salts of the prothrombin of the circulating lymph into thrombin.

In shed lymph a supply of thromboplastin is furnished by the lymphocytes, but more slowly than in the case of the blood in which the additional thromboplastin is derived from the unstable platelets (*loc. cit.*). H. W. B.

The Effect of Temperature on Thrombin and Antithrombin. W. H. Howell (*Amer. J. Physiol.*, 1914, **36**, 1—7).—At temperatures approximating to the body-temperature, the action of antithrombin is greatly augmented, and this may be a factor of importance in maintaining the fluidity of blood during life. The effect of high temperatures (60—100°) in weakening or destroying the activity of thrombin is greatly increased by the presence of neutral salts, such as sodium chloride. W. D. H.

Effect of Filtration Through a Berkefeld Filter on the Coagulability of Oxalated Plasma. C. H. Goddard (*Amer. J. Physiol.*, 1914, **35**, 333—339. Compare Cramer and Pringle, A., 1913, i, 417).—The author finds that the various proteins in oxalated plasma filter at different rates through a Berkefeld filter. The first portion of the filtrate does not contain any fibrinogen, and therefore does not clot on the addition of soluble calcium salts or of an active solution of thrombin. The last portion of the filtrate clots promptly when calcium chloride is added, whilst intermediate portions may either not clot at all on the addition of calcium salts or may show a delayed coagulation. Since the filter thus holds back, not only the suspended blood-platelets, but also the proteins concerned in the coagulation process, it follows that the views of Cramer and Pringle (*loc. cit.*) regarding the essential function of the platelets in the coagulation of the blood are not confirmed.

The plasma of oxalated lymph, which does not contain any blood-platelets, behaves, as regards the coagulation of the

successive filtrates, in the same way as oxalated blood-plasma. H. W. B.

Immunisation Against the Anticoagulating Effect of Hirudin. MIGUEL VERA and LEO LOEB (*J. Biol. Chem.*, 1914, **19**, 305—321).—A full account of work of which a preliminary note has already appeared (A., 1914, i, 617). H. W. B.

The Effect of Shaking on Serum. HANS SCHMIDT (*J. Hygiene*, 1914, **14**, 399—416).—Shaking serum with air produces coagulation and denaturation of the euglobulin, due to alteration in the surface energy of the serum leading to adsorption of albumin, thus rendering the euglobulin labile, which then coagulates and becomes insoluble. The process is not due to oxidation; it is shown that conditions which render the euglobulin more stable, such as previous heating and the presence of a hypertonic medium, tend to inhibit the effect of shaking, whereas dilution with water or storage, rendering the euglobulin labile, favours the effect of shaking. W. D. H.

Serological Tests. L. GÓZONY, E. HINDLE, and P. H. Ross (*J. Hygiene*, 1914, **14**, 354—359).—Sera and antisera kept in the dark in sealed tubes occasionally give specific reactions after twelve years. In most cases the results are negative, especially in antisera. Fowl or human blood gives specific precipitin and complement-fixation reactions after being in the alimentary canal of blood-sucking arthropods for at least twenty-three months.
W. D. H.

The Chemical Control of the Gastric Hunger Contractions. A. B. LUCKHARDT and A. J. CARLSON (*Amer. J. Physiol*, 1914, **36**, 37—46).—Blood from starving animals, and from animals without a pancreas, transfused into normal animals acts as a temporary stimulus to the gastric hunger mechanism. Excessive hæmorrhage has a similar effect. Starvation, pancreatic diabetes, and possibly large hæmorrhages, increase some substance or substances which act as stimuli to hunger contractions of the stomach. Acidosis is not responsible for the result, since injection of the acetone group of substances is ineffective in this direction.
W. D. H.

The Influence on Metabolism of Small Amounts of Thyroid Gland and of Anterior Lobe of Pituitary. JAMES ARTHUR HEWITT (*Quart. J. expt. Physiol.*, 1914, **8**, 113—124).—0·5 Gram of fresh ox thyroid per diem in an adult rat causes loss of body-weight, and increases the appetite. Double this dose lessens appetite. The smaller dose causes more retention of nitrogen than the larger. Simultaneous administration of small amounts of anterior lobe of ox pituitary has no influence on these results.
W. D. H.

The Influence on Metabolism of Small Amounts of Thyroid Gland and Posterior Lobe of Pituitary. JAMES ARTHUR HEWITT (*Quart. J. expt. Physiol.*, 1914, **8**, 297—302).—Doses less than 0·25 gram of fresh ox thyroid in a rat cause an increase of weight, and increase the appetite; a dose of 0·25 gram at first diminishes the appetite, and later increases the food consumed. The smaller dose causes a greater retention of nitrogen than the larger. Doses of 0·125 to 0·25 gram increase the excretion of ammonia in the urine, and this is still further raised by simultaneous administration of small amounts of posterior lobe of ox pituitary.

W. D. H.

Water Drinking. XX. PHILIP B. HAWK (*Biochem. Bull.*, 1914, **3**, 420—434).—Mainly a résumé of the author's previous work and conclusions; the main result is that the drinking of a reasonable amount of water with meals will promote the secretion and activity of the digestive juices, the digestion and absorption of food, will retard the growth of intestinal bacteria, and lessen the putrefactive processes in the intestine. W. D. H.

Water Drinking. XXI. Direct Demonstration of the Stimulatory Power of Water in the Human Stomach. OLAF BERGEIM, MARTIN E. REHFUSS, and PHILIP B. HAWK (*J. Biol. Chem.*, 1914, **19**, 345—371. Compare A., 1914, i, 1107).—Experiments on human subjects are described in which the variations in the acidity of samples of the contents of the stomach are determined after the ingestion of varying quantities of water.

It is found that water (ordinary or distilled), either cold or warm, is a very strong gastric stimulant, and in some cases leads to a flow of gastric juice containing, in less than twenty minutes sufficient acid to neutralise its own volume of $N/10$-sodium hydroxide. The acidity of the gastric juice secreted after water stimulation ranges from 0·18 to 0·44% of hydrochloric acid, with an average value of 0·28%. As small a volume of water as 50 c.c. is shown to have a pronounced and immediate stimulatory power in the human stomach. In the normal individual, water produces fully as great a stimulation as does an Ewald test meal, and the acidity values follow a similar type of curve.

Evidence of "latent period" or of "fatigue" could not be discovered in the case of the gastric glands of the human stomach. The flow of gastric juice sometimes continued after the water which had evoked its secretion had passed on into the intestine. The stimulatory power of the water is not influenced in a uniform way by the volume of fluid introduced into the stomach. In some instances a small volume of water gave a pronounced stimulation whereas in others the response was relatively less pronounced when a larger volume of water was employed.

The authors draw the conclusion that to drink water between meals appears to result in a waste of "glandular energy." It seems that water can best further the digestive processes when taken with, instead of between, meals. H. W. B.

Value of the Proteins of the Cereal Grains and of Milk for Growth in the Pig, and the Influence of the Plane of Protein Intake on Growth. E. V. McCollum (*J. Biol. Chem.*, 1914, **19**, 323—333. Compare A., 1913, i, 549).—The author has determined the amount of nitrogen retained by pigs fed on various grains for periods of forty to sixty days. The results show that in the young pig the growth tendency is so great that the synthesis of body protein is effected at the maximum rate possible with the particular mixture of amino-acids yielded by the food protein. The more protein given in the food, the more rapid is the growth of the animal and the larger is the absolute quantity of nitrogen retained. The constancy of the proportionate amount of ingested protein which is retained in the body at different planes of protein intake indicates that the rate of retention of nitrogen is limited by the chemical composition of the food proteins, and not by the physiological capacity of the pigs to grow.

There appears to be very little difference in the value for growth of the protein mixtures contained in the three cereal grains wheat, oat, and maize. A maximum of 23—24% of the ingested nitrogen from any one of these sources can be retained for growth. Feeding with mixtures of these grains did not lead to a greater retention of nitrogen than was attained by restricting the diet to a single source for the protein.

In two experiments in which the source of nitrogen was milk protein, the retention of nitrogen amounted to as much as 60% of the nitrogen absorbed. H. W. B.

Influence on Growth of Rations Restricted to the Maize or Wheat Grain. E. B. Hart and E. V. McCollum (*J. Biol. Chem.*, 1914, **19**, 373—395. Compare A., 1914, i, 620).—When pigs are restricted to a diet of maize meal and gluten, little or no growth is secured; but with an addition of salts, making the entire ash content of the ration very similar in quality to that of milk, approximately normal growth is attained. When the diet consists wholly of wheat, growth is again limited, with both pigs and rats. The addition of salts induces more growth, but the beneficial effect is now found to be only temporary (compare McCollum and Davis, A., 1913, i, 551). The further addition of butter-fat to the diet of wheat and salts results in the attainment of an almost normal growth. The animals remain vigorous and strong for a long period, but in some individuals a partial decline, mainly characterised by stiffness, ultimately sets in. The addition of casein to the wheat–salts–butter-fat diet secures a completely normal growth for pigs and rats. Normal reproduction, as well as normal growth, has been obtained with such rations. H. W. B.

The Digestibility of Maize Consumed by Swine. S. C. Guernsey and John M. Evvard (*Biochem. Bull.*, 1914, **3**, 369—372).—Maize was prepared in five different ways, and the food and fæces were analysed. The results are given in tabular form. Digestibility and the time required for digestion are closely correlated. W. D. H.

Toxicity of Phenolic Compounds on Amphibian Eggs. Ross A. Gortner and Arthur M. Banta (*Biochem. Bull.*, 1914, **3**, 357—368).—Amphibian eggs and embryos are killed by an 0·05% solution of "tricresol" within three days; smaller doses kill in a longer time or retard development; there is some difference of resistance between frogs' eggs and salamanders' eggs. Similar details are recorded for orcinol, resorcinol, catechol, phloroglucinol, tannin, guaiacol, tyrosine, and tyrosol. Pigment formation is inhibited by most of the reagents mentioned. Tyrosine, which is very slightly toxic, increases pigmentation. W. D. H.

The Viscosity of Bile. R. Burton-Opitz (*Biochem. Bull.*, 1914, **3**, 351—356).—Ox bile is less viscous than dog bile; the former contains only traces of mucin. High viscidity and viscosity do not, however, always go together. Lowering the temperature raises the viscosity (and the specific gravity). A slight decrease in viscosity occurs on autolysis. Tables of illustrative measurements are given. W. D. H.

The Origin of the Active Material of the Posterior Lobe of the Pituitary. P. T. Herring (*Quart. J. expt. Physiol.*, 1914, **8**, 245—266).—Any action in stimulating the uterus and milk secretion produced by extracts of the anterior lobe of the pituitary is a product of the cells of the pars intermedia; extracts of this part have very little pressor action, or action on the kidney. Repeated doses confer no immunity in reference to uterine contraction. Extracts of the pars nervosa act on blood pressure as described in previous communications on the uterus, kidney, and mammary gland. This action may be due to separate principles, but these are all formed in the pars intermedia; their hyaline secretion is stored in the pars nervosa, and may pass into the cerebro-spinal fluid. W. D. H.

The Physiological Activity of the Pars Intermedia and Pars Nervosa of the Ox-pituitary Compared. P. T. Herring (*Quart. J. expt. Physiol.*, 1914, **8**, 267—274).—The action of extracts of the pars nervosa in the uterus is from 2 to 5 times more powerful than that of extracts of the pars intermedia. The former have no action at all on blood pressure and on the kidney. This sort of evidence, although not conclusive, suggests that the actions are due to more than one substance. The substance acting on the uterus is possibly an early result of the breaking down of the product formed in the cells of the pars intermedia, and that acting on the kidney and on blood pressure is formed later.

W. D. H.

Differential Fat-Staining. E. T. Bell (*J. Path. Bact.*, 1914, **19**, 105—113).—The dichromate-Sudan III stain demonstrates fat droplets in thin paraffin or frozen sections. The annular droplets are probably triolein; the solid spheres are mainly lipoids. In most moderately fatty human kidneys the fat is chiefly lipoid; in

the liver it is chiefly triolein. In rats fed heavily on olive oil, the convoluted urinary tubules may become filled with droplets which are mainly triolein. W. D. H.

Acidosis in Omnivora and Herbivora and its Relation to Protein Storage. H. STEENBOCK, V. E. NELSON, and E. B. HART (*J. Biol. Chem.*, 1914, **19**, 399—419).—Cereal grains when hydrolysed and oxidised in the body yield a preponderance of acid radicles. On such rations, the ammonia content of the urine is high, with a compensatory fall in the output of urea. The addition of basic salts to the food is followed by a diminution in the urinary ammonia and an increase of urea. The conclusion drawn by the authors is that naturally acid rations, such as the cereal grains, if otherwise satisfactory, are as effective for growth and reproduction as those of basic character.

The ingestion of mineral acids results in a large output of ammonia to effect its neutralisation, and it is only when the amount of acid ingested is excessive that the skeleton is drawn on and decalcification of the bones takes place. On returning to a normal diet, there is a rapid storage of calcium and also of nitrogen. H. W. B.

Fasting Studies. XIV. The Excretion of Urinary Indican During Two Fasts of One Hundred Days Each. CARL P. SHERWIN and PHILIP B. HAWK (*Biochem. Bull.*, 1914, **3**, 416—419. Compare A., 1914, i, 222).—The first fast in a dog lasted 117 days, and the indican output was continuous and fairly high throughout; the second fast in the same animal lasted 105 days; the indican was less, and entirely disappeared after fifty-seven days. As previously shown, "repeated fasting" leads to greater resistance in an animal. W. D. H.

The Pressor Bases of Normal Urine. WILLIAM BAIN (*Quart. J. expt. Physiol.*, 1914, **8**, 229—241).—The pressor bases of the urine can be best separated by adsorption by charcoal, from which they can subsequently be extracted. The most abundant base present is soluble in ether and volatile with steam. It was isolated as an oxalate, which in physical characters and elementary analysis was shown to be identical with *iso*amylamine oxalate. After thorough extraction by ether, there is evidence of a second pressor base in some urines, which is, however, not tyramine. Its nature is not yet determined. The pressor effect of this second base may be preceded by a fall of pressure, which may possibly be due to Abelous' urohypotensine. Trimethylamine is not a pressor substance; such action, if present in commercial specimens, is due to impurities. W. D. H.

Metabolic Factors in Beri-Beri. I. The Effect of Increasing the Carbohydrate Ration on the Development of Polyneuritis in Birds Fed on Polished Rice. W. L. BRADDON and E. A. COOPER (*J. Hygiene*, 1914, **14**, 331—353).—In the preparation

of a dietary to obviate beri-beri, not only the amount of anti-neuritic material must be considered, but also its calorific value. Especially it is necessary to maintain a proper proportion of carbohydrate intake. The amount of antineuritic substance required increases with the quantity of carbohydrate metabolised; the precise proportion is not yet determined. W. D. H.

The Iron of Organs in Bronzed Diabetes (Hæmochromatosis). ROBERT MUIR and JOHN SHAW DUNN (*J. Path. Bact.*, 1914, **19**, 226—238).—This condition is associated with cirrhosis of the liver and pancreas. Hæmosiderin is deposited in the skin and other organs; there is a large increase of iron in the organs, especially in lymph glands, liver, and pancreas. There appears to be no increase in hæmolysis, but the source of the iron appears to be twofold, normal hæmolysis and iron from the food; the cells have an increased affinity for iron. W. D. H.

The Urinary Solids in Nephritis. JOHN P. KINLOCH (*J. Path. Bact.*, 1914, **19**, 77—101).—In the glomerular nephritis of scarlet fever and diphtheria, the water and nitrogen excreted are lessened; in interstitial nephritis this does not occur. Details are also given in reference to the salts. The glomerulus is regarded as secreting more nitrogen than has been previously assumed. The glomerulus also has a special secretory function towards chlorides, but not towards phosphates. It excretes sulphates independently of nitrogen. Nitrogen and phosphate excretion are not affected by degeneration of the tubular epithelium. Re-absorption in the tubules does not explain all the variations in chloride excretion, neither does it definitely influence the output of phosphates and sulphates. W. D. H.

Regulation of the Blood Volume in Experimental Nephritis. R. A. CHISOLM (*J. Path. Bact.*, 1914, **19**, 265—275).—Extracts made with Ringer's fluid of kidneys rendered nephritic by uranium nitrate or potassium chromate contain a substance which hinders the passage of fluid from the vessels to the tissues when infused into rabbits. This substance, which is not a coagulable protein, is absent in normal kidneys. W. D. H.

The Thermoprecipitin Method in the Diagnosis of Bubonic Plague in Cadavers. CHARLOTTE E. WARNER (*J. Hygiene*, 1914, **14**, 360—371).—This reaction between plague-immune serum and extracts of plague bacilli is specific, and can be used to diagnose plague in cadavers, but doubtful and negative reactions do not exclude plague. The method, although useful as a confirmatory reaction, can therefore not replace the usual bacteriological methods. W. D. H.

The Abderhalden Serum Test for Pregnancy. JACOB ROSENBLOOM (*Biochem. Bull.*, 1914, **3**, 373—374).—This much discussed method gave in the author's hands trustworthy results.
W. D. H.

Landau's Test for Syphilis. J. BRONFENBRENNER and J. ROCKMAN (*Biochem. Bull.*, 1914, **3**, 375—380).—This test is based on the property of syphilitic serum of combining with iodine. The test is found not to be specific, but is given frequently by normal serum. W. D. H.

Purified Antigen of Besredka in the Serum Diagnosis of Tuberculosis. J. BRONFENBRENNER and J. ROCKMAN (*Biochem. Bull.*, 1914, **3**, 375—376).—Removal of the lipoids does not affect the antigenic properties of Besredka's tuberculin. What protein or protein derivative is the really active agent is not yet determined. W. D. H.

Besredka's Tuberculin. J. BRONFENBRENNER and J. ROCKMAN (*Biochem. Bull.*, 1914, **3**, 381—385).—Further work in attempts to ascertain the active substance. The tuberculin was found to present many differences in activity in different preparations. Possibilities to explain these are discussed, but no conclusion is reached. W. D. H.

Resistance of the Vaccine Virus to Filtration. A. B. GREEN (*J. Hygiene*, 1914, **14**, 182—185).—The virus in vaccine lymph (calf) does not pass through a Berkfeld V filter; either its molecules are too large or it is contained within a substance with large molecules. It is improbable that passage through a filter destroys its activity. W. D. H.

The Effect of Radiant Energy on the Lens and Humors of the Eye. W. E. BURGE (*Amer. J. Physiol.*, 1914, **36**, 21—36).—Radiation from a quartz mercury vapour lamp intense enough to coagulate egg-albumin and similar proteins in an hour does not coagulate the proteins of the lens or of the humors of the eye, or affect their transparency, after 100 hours' exposure. The most effective region of the ultra-violet spectrum in coagulating egg-white lies around 265 $\mu\mu$. Solutions of calcium or magnesium chloride, sodium silicate or dextrose too weak to affect the transparency of the lens in themselves, modify conditions so that ultra-violet light can precipitate the lens protein and produce opacity. Lenses affected by cataract contain excess of such substances; hence the prevalence of cataract in diabetes. The same substances decrease the fluorescence of the lens. Radiation from the infra-red and visible region of the spectrum has no such effect, provided coagulation by heat is excluded. W. D. H.

Is the Antagonistic Action of Salts Due to Oppositely Charged Ions? JACQUES LOEB (*J. Biol. Chem.*, 1914, **19**, 431—443).—The author ascertains what are the concentrations of various salts which are just sufficient to prevent the formation of embryos from *Fundulus* eggs. These limits are termed the toxic concentrations, and it is found that in the presence of a given quantity of a bivalent cation, the toxic concentrations for the

various salts are altered in varying proportions. Further, the toxicity of the bivalent magnesium ion is antagonised just as easily by a univalent as by a bivalent anion. The valency of the anion does not appear to have any determining influence on the power of a salt to antagonise the toxicity of the magnesium cation. Moreover, the univalent anion in potassium chloride reduces the toxicity of the bivalent cation in magnesium chloride much more than does the multivalent anion in sodium citrate.

From these and similar considerations the author draws the conclusion that the antagonistic action of salts is not due to oppositely charged ions, but that the mixture of sodium chloride, potassium chloride, and calcium chloride, in the right proportion and concentration, has a specific membrane-forming or membrane-preserving effect on all cells, and that solutions different from this mixture have a destructive effect which is the greater the higher the concentration and the more the composition of the solution deviates from that of the optimum solution. H. W. B.

Pharmacological Study of the Aminopyridines. I. 2-Aminopyridine and its Acetyl Derivative. A. PITINI (*Ann. Chim. Applicata*, 1914, **2**, 213—217).—The toxicity of 2-aminopyridine is equal to that of stovaine, whilst 2-acetylaminopyridine is less toxic than nirvanine, but more so than novococaine. The anæsthetic effects of the two compounds are described.

T. H. P.

Pharmacological Investigations on Certain Derivatives of Morphine and Codeine. A. PITINI (*Ann. Chim. Applicata*, 1914, **2**, 208—213).—Sodium morphineoxidesulphonate and potassium codeineoxidesulphonate (compare Freund and Speyer, A., 1911, i, 909) have no pharmacological action, whilst sodium morphinesulphonate and codeinesulphonate exert, in the frog, toxic effects similar to, but less marked than, those of the alkaloids themselves.

T. H. P.

Fixation of Arsenic by the Brain after Intravenous Injections of Salvarsan. JAMES MCINTOSH and PAUL FILDES (*Proc. Roy. Soc.*, 1914, [*B*], **88**, 320—326).—The authors find, by experiments *in vitro*, that brain tissue fixes neosalvarsan as readily as does liver tissue. Moreover, injection of neosalvarsan into the cerebrospinal fluid of rabbits rapidly produces paralysis or death. The conclusion drawn is that the absence of arsenic in the brain after intravenous injections of salvarsan and neosalvarsan in man and in animals is due, not to a lack of affinity between brain tissue and the drugs, but to an inability on the part of the drugs to penetrate into the substance of the brain. It was further observed that penetration of neosalvarsan into the brain cannot be obtained by frequently repeated intravenous injections. An explanation is thus given of the lack of success which often attends the treatment of syphilitic lesions of the brain by the administration of salvarsan.

H. W. B.

Effective Principle in Thyroid accelerating Involution in Frog Larvæ. MAX MORSE (*J. Biol. Chem.*, 1914, **19**, 421—429).—The author finds that the rapid metamorphosis of tadpoles, first observed by Gudernatsch (*Arch. Entwicklungsm.*, 1912, **35**, 457) on feeding with thyroid gland, can also be accomplished by feeding with iodothyrin, iodised blood-albumin, or 3 : 5-di-iodotyrosine. Inorganic iodides, starch "iodate," and iodine-containing algæ are ineffective. The metamorphosis takes place in three days instead of requiring the normal fortnight.

The suggestion is made that the observed positive results are dependent on a rise in the opsonic index, associated with increased phagocytosis, such as is known to occur in other organisms after feeding with thyroid extract. H. W. B.

Effect of the Intramuscular Injection of Pituitary Extract on the Secretion of Milk in the Human Subject. REUBEN L. HILL and SUTHERLAND SIMPSON (*Amer. J. Physiol.*, 1914, **35**, 361—366).—The injection of pituitrin equivalent to 20 mg. of the dried infundibular portion of the gland into a female subject in lactation was followed, in ten minutes, by a marked increase in the amount of milk secreted. The milk withdrawn after the injection was rich in fat, the average figure for three experiments being 5·5%, as compared with 3·4% for three days when no pituitrin was administered. In the milk yielded twenty-four hours after injection, the fat content was still somewhat above the normal. Although no quantitative estimations were made, it would appear that the quantity of milk secreted naturally on the morning after the injection was less than normal. H. W. B.

The Effect of Pituitary Extract on Milk Secretion in the Goat. REUBEN L. HILL and SUTHERLAND SIMPSON (*Quart. J. expt. Physiol.*, 1914, **8**, 103—112).—Subcutaneous or intravenous injection of ox-pituitary extract into the goat produces a marked increase of milk secretion when the milking is performed fifteen minutes after the injection; the next milking, several hours later, shows a corresponding decrease. In the first milking, the milk fat (but not the other solids) is increased, but no sudden fall in the fat was observed (as stated by Hammond) at the second milking.
W. D. H.

Bleached Flour. FRANK L. HALEY (*Biochem. Bull.*, 1914, **3**, 440—443).—Experiments on guinea-pigs lead the author to the conclusion that although nitrite is present, it is not enough in quantity to cause the formation of methæmoglobin, and that bleached flour is not detrimental to health. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Nitroso-Bacteria. H. S. FREMLIN (*J. Hygiene*, 1914, **14**, 149—162).—The nitroso-bacterium grows readily in or on ammonia agar, especially if 5 or 10% of beef broth is added. Potassium phosphate agar containing bouillon gelatin, but not ammonia, also leads to the formation, first of ammonia and then of nitrite. Urine is also a good culture medium, so also are peptone water, peptone beef broth, and milk or blood-serum. The nitroso-bacterium is a powerful nitrite-forming organism; it is not readily destroyed, and a certain amount of organic matter is essential to its better development. W. D. H.

Purification of Silk Peptone for Bacteriological Purposes. I. WALKER HALL (*J. Path. Bact.*, 1914, **19**, 286—304).—The tetrapeptide sold as silk-peptone has certain advantages for bacteriological purposes over complex mixtures like Witte's peptone. Methods are described for purifying the crude product; the pigment may be removed by filtration through *Argilla alba*. The product has the same optical rotation and amino-acid content as that obtained by phosphotungstic acid precipitation. W. D. H.

Organisation of the Cell with Respect to Permeability. W. J. V. OSTERHOUT (*Science*, 1913, **38**, 408—409).—When cells of the marine alga *Griffithsia* are placed in hypertonic sea water, a withdrawal of water takes place and the protoplasmic sack contracts; on replacing the cells in sea water, the sack expands to its original size. With hypertonic ammonium chloride, the sack also contracts, but the inner wall contracts much more than the outer wall; so that there are two surfaces, the outer (plasma membrane) and the inner (vacuole wall), which do not act in the same way with respect to permeability. This may be due to the outer surface being more permeable to ammonium chloride, and partly to a change in permeability produced by the salt.

With more dilute ammonium chloride there is a marked contraction of the inner surface alone.

As protoplasm is composed of a variety of structures, it seems possible that many kinds of semi-permeable surfaces exist within the cell. N. H. J. M.

Effect of Alkali on Permeability. W. J. V. OSTERHOUT (*J. Biol. Chem.*, 1914, **19**, 335—343).—The author has determined the effect on the electrical resistance of the addition of small amounts of sodium hydroxide to solutions containing the living tissues of *Laminaria saccharina*. Concentrations of sodium hydroxide greater than 1/1000*N* lead to a diminution in the electrical resistance, and the author draws the conclusion that concentra-

tions of sodium hydroxide below $1/1000N$ do not have any effect on the permeability of the cell walls, whilst above this limit the permeability is increased, associated with injury of the cells if the exposure is sufficiently prolonged, but not when the exposure is short. H. W. B.

Chemical Dynamics of Living Protoplasm. W. J. V. Osterhout (*Science*, 1914, **39**, 544—546).—An experiment in which living tissue of *Laminaria* was placed in $0{\cdot}52N$ sodium chloride, which has the same conductivity as sea water, and the electrical resistance measured every ten minutes, showed a rapid fall from 980 to 320 ohms in 200 minutes, when the cells were killed. The results showed that the rate of the reaction was almost constant, indicating that the sodium chloride reacted with one substance, so little of it being used up that its concentration changed only slightly. The loss of resistance might also be due to the spontaneous change of some substance in the protoplasm, a process which goes on with extreme slowness until catalysed by the sodium chloride. This implies that even in a healthy and living cell the process of death is always going on. N. H. J. M.

Vitality and Injury as Quantitative Conceptions. W. J. V. Osterhout (*Science*, 1914, **40**, 488—491).—The vitality of a tissue is so dependent on the maintenance of its normal permeability that the permeability of protoplasm may be employed as a sensitive and trustworthy indicator of its vitality, and this may be done by estimating the electrical resistance. In this way a quantitative treatment of injury becomes possible. The degree of injury may be defined as the amount, expressed as percentage of the normal net resistance, by which the resistance falls below the normal.

The method of plasmolysis may be used, not only to distinguish between living and dead cells, but between cells of normal vitality and those in which vitality is impaired. N. H. J. M.

Quantitative Criteria of Antagonism. W. J. V. Osterhout (*Bot. Gaz.*, 1914, **58**, 178—186).—The best criteria of antagonism are obtained by mixing equally toxic solutions, as the effect of each mixture, if there is no antagonism, is known at the outset. Mixtures of two equally toxic solutions must have the same effect as the pure solutions themselves if the effects of the salts are additive. Where antagonism exists, there is increased growth, and the amount of the increase, expressed as percentage of the growth in pure solutions, is the most satisfactory measure of antagonism.

It is desirable to employ uniform seeds; and only such portions of the plants as are in contact with the solution should be measured. N. H. J. M.

Measurement of Antagonism. W. J. V. Osterhout (*Bot. Gaz.*, 1914, **58**, 272—276).—It is shown that the measurement of antagonism in solutions containing more than two components pre-

sents no difficulty when equally toxic pure solutions are mixed. Methods for the graphical expression of antagonism in mixtures of three or more components are suggested. N. H. J. M.

Forms of Antagonism Curves as Affected by Concentration. W. J. V. Osterhout (*Bot. Gaz.*, 1914, **58**, 367—371).—It was found with antagonism curves of different types, that dilution of the solutions to half strengths results in very marked alterations in the form of the curve. An example given of four curves obtained with different dilutions shows that as the solution becomes more dilute, the curve becomes flatter, so that finally a straight line would be obtained. The two ordinates at the ends of each curve are equal in height, showing that the pairs of pure solutions were in each case equally toxic.

A solid model is described which gives a complete description of the changes in the antagonism curve as dilution increases.

Strong solutions usually furnish a much more satisfactory criterion of antagonism than weak solutions. N. H. J. M.

Creatinine in Leguminous Seeds. K. Oshima and M. Ariizumi (*J. Coll. Agric. Tohoku Imp. Univ.*, 1914, **6**, 17—25).—Creatinine was found in seeds of Adzuki beans, kidney and soja beans, and, in smaller amounts, in horse beans and green peas. N. H. J. M.

Occurrence and Significance of Manganese in the Seed Coat of Various Seeds. J. S. McHargue (*J. Amer. Chem. Soc.*, 1914, **36**, 2532—2536).—During an investigation on the occurrence of barium in plants (A., 1913, i, 809), the author observed the presence of manganese in the ash of hazel-nut shells. Several nuts and seeds have now been examined, and it has been found that manganese is of very general occurrence. The amount of manganese present varies considerably in different parts of the same seed, and the seed coat surrounding the kernel contains a much larger proportion than the kernel or the outer coats. Experiments are recorded which show that there is a close connexion between the amount of manganese and the presence of oxydases in plant tissues, and it is therefore considered probable that the accumulation of manganese in the seed coat bears an important relation to the vital processes in seed formation and germination. E. G.

Oxydases of Acid Tissues. G. B. Reed (*Bot. Gaz.*, 1914, **57**, 528—530).—The acid tissues of *Citrus* fruits contain oxydases, which are evidently protected in some way from the action of the acid. It is suggested that the protection may be afforded by a semipermeable tissue through which the acid cannot pass. It seems evident that the membranes are not normally permeable to acid, because lemon seeds frequently germinate while in the carpels; in lemon juice, even when several times diluted, they fail to germinate. N. H. J. M.

Bitter Principle of Common Ragweed. BURT E. NELSON and GEORGE W. CRAWFORD (*J. Amer. Chem. Soc.*, 1914, **36**, 2536—2538).—An examination has been made of the common ragweed (*Ambrosia artemisifolia*). Two substances have been isolated, one, m. p. 208°, crystallising in white needles or prisms, and the other, m. p. 65—70°, an amber-coloured, amorphous substance. The former is tasteless and physiologically inactive, whilst the latter has a bitter taste, and is probably identical with absinthin from wormwood. It is considered that there are no reasonable grounds for administering ragweed preparations for hay-fever. E. G.

Oxidation by Catalysts of Organic and Inorganic Origin. ALFRED J. EWART (*Proc. Roy. Soc.*, 1914, [*B*], **88**, 284—320. Compare Moore and Whitley, A., 1909, i, 623).—The author has investigated the action of the oxydases of the apple, potato, carrot, parsnip, beetroot, orange, and lemon, and of the inorganic salts of copper, iron, chromium, manganese, lead, etc., on guaiacum, *p*-phenylenediamine, quinol, pyrogallol, gallic acid, tannic acid, and tyrosine. The correspondence between the action of these organic and inorganic catalysts is found to be extremely close. Both classes of catalysts may be accelerated in the presence of sensitisers, such as sodium or potassium chloride or phosphate, or retarded or prevented by a variety of inhibitory substances (barium chloride, sodium fluoride, organic and inorganic acids). With increasing concentration, an accelerating substance may become inhibitory, whilst a substance which accelerates the action of one oxydase may antagonise the action of another.

Strong metallic poisons will arrest the action of organic oxydases and destroy them if immediate contact or rapid penetration is assured. The pulp of apples turns brown when soaked in bulk in metallic poisons, because the slowness of penetration allows the cell to be killed and browning to occur before the oxydase is destroyed. Any poison which destroys the oxydase also removes the power of turning brown. The browning is due to the action of the oxydase on a compound of tannic acid in the apple pulp. In the potato, the oxydase acts on a compound of tyrosine.

The oxydases of the beetroot and potato appear to be related to one another, and to be among the strongest plant oxydases, the nearest analogies to them being ferric salts and ferricyanides. The apple, carrot, and parsnip contain oxydases of the same type, but of a feebler grade.

The author considers that oxydases and peroxydases do not constitute distinct classes of enzymes. A peroxydase is regarded as a weak or attenuated oxydase. Strong oxydases cause direct oxidation from the oxygen dissolved in a watery solution; weak oxydases can only use the oxygen from labile oxygen compounds, such as hydrogen peroxide, or dissolved oxygen in the presence of sensitisers, such as the chlorides or phosphates of sodium or potassium. Various intermediate grades of activity occur. An oxydase may be a "peroxydase" to certain oxidising agents, or may

become so when attenuated. The supposed separation of oxydase and "peroxydase" by fractional precipitation with alcohol may be merely the result of attenuation.

Attention is drawn to the influence which sensitising substances may have on special oxidations and on respiration in general. It is suggested that they exert a stimulatory or controlling action on plant metabolism, and that the sodium chloride always present in the ash of plants may have special significance in this connexion. This view also explains why small doses of salt stimulate the growth of many plants, and why phosphates, in addition to being food substances, act as stimuli to growth. The stimulating action of many metallic salts on growth may be due to their functioning as oxydases.

Exposure of apple or potato pulp to the action of ether or chloroform leads to a gradual diminution in the activity of the oxydases present. Chloroform attenuates the oxydases more rapidly than ether does.

Ursol tartrate turns lignified walls red or reddish-brown. This is not an oxydase reaction, but is an admirable test for lignin, especially valuable for demonstrating the wood elements in pulpy tissue. H. W. B.

Effect of Salicylaldehyde on Plants. J. J. Skinner (*Biochem. Bull.*, 1914, **3**, 390—402).—Full details are given of the harmful effect produced by various concentrations of salicylaldehyde when added to soil or solution cultures; wheat, maize, rice, and other plants were employed. The action is not attributable to acidity; calcium carbonate appeared to ameliorate the effects. W. D. H.

The Phosphoric Oxide Content of Maize Flour. J. McCrae (*J. Hygiene*, 1914, **14**, 395—398).—Fraser and Stanton have suggested that the estimation of phosphoric oxide in rice may be usefully employed as a criterion of the amount of vitamine present, the two substances running approximately parallel in amount. Analyses of maize are given here which show that in the conversion of the grain into flour a loss of phosphoric oxide occurs; concomitantly, it is assumed there is a loss of vitamine. The loss is not so great as in the process of rice polishing. Improved processes of milling in the Transvaal have still further reduced the loss. The miners certainly are in better health who use the flour made this way. W. D. H.

Saccharogenesis in Beetroot. H. Colin (*Compt. rend.*, 1914, **159**, 687—689. Compare Girard, A., 1884, 476; 1885, 75).—An endeavour to determine the form of sugar which passes from the leaves to the roots of the beet, and is there stored as sucrose. At all stages in the growth of the plant the author finds a certain amount of reducing sugars in the roots, the amount diminishing as the plant matures. The disappearance of the sucrose from the leaves during the night is not necessarily due to migration to the

root, since it similarly disappears from detached leaves kept in the dark, with their stems in distilled water; the water does not contain a trace of sugar at the end of the experiment. Further, an examination of the petiole at its base, where it joins the neck of the root, shows that the ratio of reducing sugar to sucrose is always much greater than unity. Contrary to the views of Girard (*loc. cit.*), the author considers that the root receives from the leaf both sucrose, which it stores, and reducing sugars, which it polymerises, the entrance of these two types of sugar being regulated by the osmotic pressure of each in the mixture. The amounts of the respective sugars formed in the leaves and taken up by the roots vary with different varieties of beetroot. W. G.

Variation in the Nitrate Content of the Soils in Scania, Sweden. M. WEIBULL (*Bull. Agric. Intell. Plant Diseases*; *K. landtbr. Handl. Tidskr.*, 1914, **53**, 65—73).—Nitrates were estimated at intervals of seven to ten days, from 1907 to 1911, in the soil of a field on which different crops were grown successively; from 1909 to 1911, estimations were also made in soil from fallow land. As regards the cropped plots, those under beet contained up to 14 per million of nitrogen as nitrates; under wheat and peas, 8—9; and under grass, only 1·5 per million. On fallow land the amount rose to 33 per million. When the grass was ploughed up, the nitrates increased up to November (N = 21 per million). This was followed by a fall, due to assimilation by the succeeding wheat crop, and to loss in drainage. In the spring the amount of nitrates was low, and in the early summer there was an increase both in nitrification and assimilation.

To ascertain the effect of vegetation and cultivation, a grass plot was divided into three portions, one of which remained under grass, whilst the second was freed from vegetation, and the third dug to a depth of 30 cm. On the grass soil the nitrogen as nitrates averaged 2·4 per million, on the second portion 6·5, and on the third 11·3 per million. The amount of moisture in the second and third divisions was about equal, being about 1·5—2% higher than in the grass soil.

In order to ascertain whether it is possible to detect the point at which nitrogenous manuring becomes necessary, nitrates were estimated during July and August in eight unmanured plots growing sugar beet. The yields were estimated both on the unmanured and on manured plots. Indications were obtained that where the nitrogen as nitrates fell to 2 per million by the end of July, applications of nitrogenous manures resulted in a fairly large increased yield. With a later fall in nitrates, the effect of nitrogenous manures is less. Similar results were obtained with other crops. N. H. J. M.

Nitric Nitrogen Content in the Country Rock. ROBERT STEWART and WILLIAM PETERSON (*Utah. Agric. Coll. Exper. Stat. Bull.* 1914, **134**).—The results of analyses of numerous samples of Cretaceous and Tertiary soil-forming materials, and some of

Jurassic origin, confirmed the view that the abnormally high amounts of nitrates which sometimes occur in Utah and Colorado soils are derived from the brackish waters of the old Cretaceous and Tertiary inland seas.

The average amounts of sodium nitrate found in the different materials were as follows:

	Sandstone.	Shale.	Clay.	Ash.	Alkali.
Cretaceous.....	0·055%	0·104%	0·039%	0·870%	0·074%
Tertiary.....	0·074	0·147	0·053	0·236	0·021
Jurassic.....	0·008	0·005	—	0·175	0·017

Many of the shales and sandstones contained as much nitrate as the "nitre spots" in the cultivated soil; and calculations based on the average amount of nitrates in fifty-eight shales show that the Cretaceous shale exposed from Palisades, Colorado to Emery, Utah, contain 90 million tons of sodium nitrate. The conclusion is drawn that the nitrate deposits in Colorado, Utah, and Wyoming are far greater than those of Chile, although, so far as is known, it is nowhere in sufficient concentration to be worked.

N. H. J. M.

Comparison of Silicates and Carbonates as Sources of Lime and Magnesia for Plants. W. H. MacIntire and L. G. Willis (*J. Ind. Eng. Chem.*, 1914, **6**, 1005—1008).—The long-continued effects of liming in small or moderate amounts are to be attributed to the conservation of lime as silicates, and not to the carbonate remaining unchanged. Untrustworthy methods for the estimation of carbonates will indicate their presence in soils where none exists. Calcium silicate hydrolyses in the soil and acts like calcium carbonate, furnishing lime to the soil solution. With the exception of phosphates, calcium exists in soils almost entirely in the form of silicates; magnesium also exists as silicate. Large quantities of magnesium carbonate have a toxic effect on plants, whilst the equivalent amount of magnesia applied as finely-ground serpentine is beneficial. Calcium and magnesium silicates, wollastonite and serpentine, applied separately or together, are very beneficial to plants, and calcium silicate is decidedly superior to calcium carbonate.

W. P. S.

Manuring Experiments with Manganese Sulphate and Carbonate. G. D'Ippolito (*Ann. Chim. Applicata*, 1914, **2**, 342; from *Staz. sperim. agrar. ital.*, 1914, **67**, 621).—Experiments on the manuring of wheat and lucerne with: (1) manganese sulphate; (2) a fertiliser containing 15% of manganese sulphate; (3) natural manganese carbonate containing 35% of the pure carbonate; and (4) manganese carbonate as in (3), but containing 11% of phosphoric oxide, show that the addition of manganese gives increased yields.

T. H. P.

Organic Chemistry.

Absorption of Gasolene Vapours in Natural Gas by Fuming Sulphuric Acid. R. P. Anderson and C. J. Engelder (*J. Ind. Eng. Chem.*, 1914, **6**, 989—992).—Fuming sulphuric acid has a distinct absorbing action on certain specimens of natural gas, the absorption increasing with the amount of higher hydrocarbons, particularly gasolene vapours, present in the gas. The average number of carbon and hydrogen atoms per mol. of hydrocarbon absorbed by fuming sulphuric acid (and consequently the average molecular weight of the hydrocarbons) may be calculated from the composition of the gas before and after absorption and from the decrease in volume which takes place. Application of this reagent to the study of natural gases for the production of gasolene may be made by determining the absorption under certain uniform conditions; the composition of the portion which is absorbed should also be ascertained as a check on the indications obtained from the decrease in volume. W. P. S.

Preparation of α-Chloro-ε-bromopentan-β-ol and of a Ketone Therefrom. Eli Lilly & Co. (U.S. Pat. 1114734 and 1114735; from *J. Soc. Chem. Ind.*, 1914, **33**, 1171).—Magnesium (1 atom.) is dissolved in an absolute ethereal solution of ethylene dibromide, and epichlorohydrin (1 mol.) is added; treatment with a suitable acid produces *α-chloro-ε-bromopentan-β-ol*, $CH_2Cl\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CH_2Br$.

The *ketone*, $CH_2Cl\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2Br$, is obtained by the oxidation of the preceding carbinol, for example, with potassium dichromate and sulphuric acid. C. S.

A Comparison Between the Molecular Weights of Protagon and of the Phosphatide and Cerebrosides Obtainable from it. Alexander Lyall Pearson (*Biochem. J.*, 1914, **8**, 616—627).—The long-continued argument whether protagon is a mixture or a compound is approached by attempts to determine the molecular size of protagon and its constituents (cerebrosides and sphingomyelin). If it is a compound, the molecular size of protagon would be greater than that of its constituents; it should therefore produce little or no elevation of the boiling point of a solvent. The solvent used was chloroform. In two experiments there was no alteration in the boiling point, in one a lowering of 0·05°. Various mixtures of the cerebrosides, with or without sphingomyelin, produced elevations of the boiling point of the same solvent of 0·03°, 0·13°, 0·04°, 0·07°, 0·07°, 0·03° and 0·02° in a series of experiments. The conclusion is drawn that the protagon molecule is very much larger than that of its constituents and therefore that protagon is a compound and not a mixture of them. It is termed a phospho-cerebroside. The question whether protagon is a mixture of several phospho-cerebrosides still remains to be settled. Cramer calculated that protagon has a molecular weight of 5778 from its sulphur-content. The molecular weights of cerebro-

sides and of sphingomyelin are about 1000; one gram of a substance of this molecular weight would in a 4% solution in chloroform elevate the temperature of the boiling point of chloroform 0·10°. The smaller figures obtained in most of the experiments cited would rather tend to emphasise the author's admission that determinations of molecular weights of substances of high molecular weight can only be approximate. W. D. H.

The Dissociation of $CH_3 \cdot SO_2Cl$ and $C_2H_5 \cdot SO_2Cl$ by Aluminium Chloride. J. Böeseken and H. W. van Ockenburg (*Rec. trav. chim.*, 1914, **33**, 317—323. Compare A., 1913, i, 334).—When methanesulphonyl chloride is mixed with aluminium chloride at the ordinary temperature, in the absence of a solvent, a crystalline additive *compound*, $CH_3 \cdot SO_2Cl, AlCl_3$, is formed. On warming this compound, sulphur dioxide and methyl chloride are evolved and the aluminium chloride remains behind. If the methanesulphonyl chloride is added to the aluminium chloride in the presence of an excess of benzene, hydrogen chloride is evolved and phenyl methyl sulphone, m. p. 88°, is formed.

Ethanesulphonyl chloride behaves similarly with aluminium chloride in the absence of a solvent, giving an additive *compound*, $C_2H_5 \cdot SO_2Cl, AlCl_3$, which on warming gives ethyl chloride and sulphur dioxide, and at the same time a brown, resinous product formed by the reaction of the aluminium chloride with hydrogen chloride and ethylene, products of a secondary decomposition of the ethanesulphonyl chloride. W. G.

The Walden Inversion. Cecil L. Horton (*Chem. News*, 1915, **111**, 29—31).—In a previous paper (A., 1913, ii, 743) attention has been drawn to the directive action of the carboxyl group in the Walden reaction. This influence of the carboxyl group, together with the fact that all the substituents and reagents are unsaturated, is made the basis of a further attempt to explain the reaction in question. The theory assumes the formation of an intermediate compound in which the position of the addendum depends on the attractive or repulsive action of the carboxyl or ester group. This position determines the distribution of the valency and the resulting cleavage. The author illustrates the supposed action by reference to a number of special cases. H. M. D.

Preparation and Hydrolysis of Ethyl Hydracrylate. W. A. Drushel (*Amer. J. Sci.*, 1915, [iv], **39**, 113—121).—A convenient method for the preparation of hydracrylic acid is described, in which glycerol is oxidised by means of fuming nitric acid and glyceric acid liberated from the calcium salt by the addition of oxalic acid. The glyceric acid is converted into β-iodopropionic acid by treatment with iodine and solid yellow phosphorus, and the concentrated solution of the sodium salt is then acted on in the cold with silver oxide, using a mechanical stirrer.

Esterification of the acid with absolute alcohol leads to the formation of a mixture of acrylic and hydracrylic esters even if only very small quantities of mineral acid are present, but ethyl hydracrylate is

readily obtained if the acid is boiled with an excess of absolute alcohol in presence of anhydrous copper sulphate and mineral acids are rigidly excluded. It has b. p. 95—96°/20 mm., D^{20} 1·059, and is completely miscible with water. In the absence of a catalyst, it is hydrolysed only very slowly by water.

In presence of 0·1*N*-hydrochloric acid, the velocity coefficient ($k . 10^5$) for the hydrolysis was found to be 16·25 at 25°, 40·65 at 35°, and 98·75 at 45°. The influence of the hydroxyl group in the β-position on the rate of hydrolysis is shown by a comparison of the coefficients at 25° for ethyl propionate (71·2), ethyl lactate (76·1), ethyl hydracrylate (16·25), and ethyl glycerate (18·5). Substitution of the hydroxyl group in the β-position has therefore a marked retarding influence on the rate of hydrolysis in presence of acids.

The velocity of saponification of the ester by sodium hydroxide was also measured at 0° and 25°. The velocity coefficient 1·83 at 0° is compared with the corresponding values for ethyl propionate (1·16), ethyl lactate (14·6), and ethyl glycerate (9·02). From there numbers it is evident that the relations differ in some respects from those exhibited by the coefficients for hydrolysis by acids, but are in general agreement with the results obtained in the saponification of the esters of other oxy-acids (compare Dean, A., 1913, ii, 187). H. M. D.

α-Sulphopropionic Acid and its Resolution into Optically Active Isomerides. A. P. N. Franchimont and H. J. Backer (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 653—658).—α-Sulphopropionic acid, hitherto known only in the form of a viscous syrupy liquid, has been obtained in the form of large hygroscopic crystals containing one molecule of water of crystallisation. When dried over phosphoric oxide, it has m. p. 100·5°.

Previous attempts to resolve the acids have given negative results, but it is found that if an aqueous solution of the acid is evaporated with an equimolecular quantity of strychnine, crystals of the strychnine hydrogen salt of the dextro-acid are obtained, which may be purified by recrystallisation. From this the neutral barium salt is obtained by decomposition with barium hydroxide, and an aqueous solution of the free acid is obtained from this by addition of sulphuric acid. The solution, concentrated in a vacuum over phosphoric oxide, does not crystallise spontaneously, but crystals were obtained on the addition of a trace of the racemic compound. The acid is exceedingly hygroscopic, m. p. 81—82°, and contains one molecule of water.

The measurement of the rotatory power of the acid and its salts gave the following values for $[M]_D^{20}$: *d*-acid +49·2°, potassium hydrogen salt +45·7°, barium hydrogen salt +79·8°, strychnine hydrogen salt −71·4°, normal barium salt −14·4°. The lævo-acid was not obtained in perfectly pure condition, but the following data are recorded: *l*-acid −45·8°, strychnine hydrogen salt −135°, normal ammonium salt +14·8°.

It is noted that the molecular rotatory power of α-sulphopropionic acid is greater than that of α-bromopropionic acid (44·4°), although the weights of the substituents are practically identical.

H. M. D.

Preparation of Acetaldehyde from Acetylene. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (Fr. Pat. 469497; from *J. Soc. Chem. Ind.*, 1915, **34**, 49).—Acetylene is passed into a solution or suspension of an organic sulphonic acid and a mercury compound, or of a mercury salt of a sulphonic acid. In either case, a free mineral acid may be added. For example, 21·6 parts of mercuric oxide are heated with 417 parts of *o*-chlorophenolsulphonic acid and 583 parts of water, and acetylene is passed into this solution at 30—35°; when the absorption of the gas has diminished considerably, the aldehyde is removed by heating or by means of steam. The yield is about 300 parts. Solutions of sulphonic acids have a high power of hydration, considerably greater than that of solutions of mineral acids of the same acidity.

C. S.

Synthesis by means of Mixed Organo-metallic Derivatives of Zinc Polyhalogenated Ketones. E. E. BLAISE (*Bull. Soc. chim.*, 1914, [iv], 15, 728—737. Compare A., 1914, i, 1050, 1051).—Certain dichloro- and trichloro-ketones have been prepared through the intermediary of *cyclo*acetals. For the preparation of these *cyclo*acetals, lactic acid, α-hydroxyhexoic acid and α-hydroxy*iso*butyric acid were tried, the last-named being the most satisfactory. Dichloroacetyl chloride condenses with lactic acid, giving *α-dichloroacetoxypropionic acid*, $CHCl_2\cdot CO\cdot O\cdot CHMe\cdot CO_2H$, m. p. 67°, b. p. 164—167°/17 mm., yielding an *acid chloride*, b. p. 116°/21 mm.; and with α-hydroxyhexoic acid giving *α-dichloroacetoxyhexoyl chloride*, b. p. 147—149°/26 mm. Dichloroacetyl chloride is best condensed with α-hydroxy*iso*butyric acid by heating the mixture on a water-bath until the action is complete, when, on cooling, *α-dichloroacetoxyisobutyric acid*, m. p. 95°, crystallises out; it is moderately readily hydrolysed by water. It gives an *anilide*, needles, m. p. 99—100°, and a *chloride*, a colourless, dense liquid, b. p. 103°/12 mm. This chloride condenses with zinc ethyl iodide in dry toluene, giving the cyclo*acetal*,

$$CHCl_2\cdot CEt\begin{matrix}O\cdot CMe_2\\ |\\ O\cdot CO\end{matrix},$$

m. p. 51°, b. p. 236—239°, or 124·5—125°/16 mm. On boiling this *cyclo*acetal with a mixture of acetic and hydrochloric acids, it is decomposed, giving a mixture of *dichloromethyl ethyl ketone*, $CHCl_2\cdot COEt$, b. p. 138·5—139° or 56·5°/36 mm., yielding with hydroxylamine glyoxaldioxime and chloromethyl chloroethyl ketone, $CH_2Cl\cdot CO\cdot CHClMe$, b. p. 60°/13 mm. (compare Vladesco, A., 1891, 1183), the second ketone being formed by migration of the chlorine atom, after the formation of the first ketone.

Trichloroacetyl chloride condenses with α-hydroxy*iso*butyric acid, giving *α-trichloroacetoxyisobutyric acid*, $CCl_3\cdot CO\cdot O\cdot CMe_2\cdot CO_2H$, m. p. 117°, giving a *chloride*, b. p. 107°/13 mm. or 113°/18 mm., and an *anilide*, m. p. 100°. The chloride yields with zinc methyl iodide the cyclo*acetal*, $CCl_3\cdot CMe\begin{matrix}O\cdot CMe_2\\ |\\ O\cdot CO\end{matrix}$, m. p. 98—99° with sublimation, which, on boiling with the mixture of acetic and hydrochloric acids, gives methyl trichloromethyl ketone, a colourless mobile liquid, b. p.

57°/48 mm., 60°/54 mm. and 134° (compare Schlotterbeck, A., 1909, i, 533). It yields a *semicarbazone*, m. p. 140°. The author agrees with Cloez that the ordinary trichloroacetone consists almost entirely of $\alpha\alpha\gamma$-trichloropropanone. W. G.

Structure of the Two Methylglucosides; a Third Methylglucoside. Emil Fischer (*Ber.*, 1914, **47**, 1980—1989).—Nef's statement (A., 1914, i, 490) that α- and β-methylglucosides are structurally different, as also are the corresponding α- and β-penta-acetyldextroses, is not in harmony with the following properties of the compounds (i) The penta-acetates are converted into the same β-acetochloro(or bromo)-dextrose by hydrogen chloride (or bromide). (ii) Treatment of β-acetobromodextrose with silver nitrate and sodium yields an acetonitrodextrose which is converted merely by crystallisation into the isomeric, stable, well-known acetonitrodextrose. (iii) By hydrolysis, Purdie and Irvine's tetramethyl α- and β-methylglucosides (T., 1903, **83**, 1021; 1904, **85**, 1049; 1905, **87**, 1022) are converted into the same tetramethyl glucose. The latter retains its methyl groups against the attack of hydrogen chloride in benzene at 105—115°, and yet is converted by methylation into the original tetramethyl α- and β-methylglucosides. A structural difference in the methylglucosides, therefore, appears to be impossible, at all events in the sense of Nef's conception.

The reaction between α-dextrose and methyl alcohol containing 1% of hydrogen chloride yields, in addition to the two crystalline methylglucosides, a considerable amount of a syrup, which has hitherto not been purified and has been regarded as dextrose dimethylacetal. It is now found that the syrup distils without decomposition in a high vacuum. The purified *substance*, $C_7H_{14}O_6$, b. p. 200—215°/0·2 mm., $[\alpha]_D^{18} - 3{\cdot}64°$ in about 10% aqueous solution, is named *γ-methylglucoside* (the prefix does not refer to the structure of the compound, but is used simply to differentiate it from the α- and β-isomerides). It is stable to alkalis, Fehling's solution, or hot water, but is hydrolysed to dextrose and methyl alcohol by *N*-acetic acid at 100°, by *N*/100-hydrochloric acid at 100°, and by *N*/10-hydrochloric acid at 17—18°. γ-Methylglucoside is scarcely attacked by emulsin or by yeast extract at 37°. C. S.

New Compounds of the Choline Type. Preparation of the Monoacetate of β-Methylbutane-$\alpha\beta$-diol. III. G. A. Menge (*U. S. Hyg. Labor., Bull. No.* **96**, 37—50. Compare A., 1912, i, 74, 949).—The physiological activity of choline and β- and γ-homocholines and their derivatives indicates that the greatest activity and the least toxicity are obtained in those compounds which contain the trimethylamine nucleus, and in which the alcoholic hydroxyl group is not further removed from the nitrogen than the β-position. Consequently, the substitution of the hydrogen atoms in the α- and the β-positions of the carbon chain by alkyl and other groups, rather than the direct extension of the chain, is indicated as the most promising development from the point of view of physiological activity.

The preparation and properties of α-methylcholine, "β-homocholine,"

"γ-homocholine," and of some of their derivatives have been already recorded (*loc. cit.*). Pure β-methyl-β-ethylcholine chloride,

$$OH\cdot CMeEt\cdot CH_2\cdot NMe_3Cl,$$

has now been prepared from the crude substance by means of the *platinichloride*. *β-Phenyl-β-methylcholine chloride*,

$$OH\cdot CPhMe\cdot CH_2\cdot NMe_3Cl,$$

colourless, rhombohedral plates, is prepared by heating β-chloro-α-hydroxy*iso*propylbenzene with a small excess of 33% alcoholic trimethylamine in a sealed tube in boiling water; it forms a *platinichloride*, $(C_{12}H_{20}ON)_2PtCl_6$, decomp. 223·5—224° (corr.), and *aurichloride*, m. p. 137·5—138·5° (corr.).

In striking contrast to all other attempts to acylate ββ-disubstituted cholines, the *acetyl* derivative of ββ-dimethylcholine chloride,

$$OAc\cdot CMe_2\cdot CH_2\cdot NMe_3Cl,$$

a colourless, waxy substance, is readily obtained by gently boiling ββ-dimethylcholine chloride with acetic anhydride and pouring the cooled mixture into dry ether; the *platinichloride* has decomp. 233—234°. The *acetyl* derivative of β-phenyl-β-methylcholine chloride, prepared by means of acetyl chloride at 100°, forms a yellow *platinichloride*.

For the preparation of α-mono- and di-substituted cholines, chlorohydrins of the types $CHRCl\cdot CH_2\cdot OH$ and $CRR'Cl\cdot CH_2\cdot OH$ are necessary. Two methods of preparing the latter, namely, (i) the addition of hypochlorous acid to olefines, and (ii) reactions indicated in the scheme:

$$CH_2Cl\cdot CRR'\cdot OH \longrightarrow OAc\cdot CH_2\cdot CRR'\cdot OH \longrightarrow OAc\cdot CH_2\cdot CRR'Cl \longrightarrow OH\cdot CH_2\cdot CRR'Cl,$$

have not been practically successful. However, the first stage of the second method, for example, heating anhydrous potassium acetate and α-chloro-β-methylbutan-β-ol to gentle boiling, readily yields the acetate, $OAc\cdot CH_2\cdot CMeEt\cdot OH$, b. p. 92·8—93°/15 mm. (Kling gives 145—147°/10 mm.), D^{25} 0·9989. C. S.

Action of Water Vapour on Barium Cyanide. Luigi Rolla (*Ann. Chim. Applicata*, 1914, **2**, 301—304).—The author has analysed the gaseous products formed by the action of water vapour on barium cyanide at various temperatures ranging from 100° to 500°. At temperatures below 200°, the changes taking place are expressed by the equations: (1) $Ba(CN)_2 + 3H_2O = Ba(OH)_2 + 2NH_3 + 2CO$ and (2) $Ba(OH)_2 + 2CO = (H\cdot CO_2)_2Ba$. In accord with the thermochemical data, the absorption of carbon monoxide by barium hydroxide occurs more readily at 100° than at higher temperatures.

At 250°, the barium formate begins to undergo partial decomposition, thus: (3) $(H\cdot CO_2)_2Ba = BaCO_3 + H_2 + CO$, and the oxalate, which is also formed to some extent, is probably decomposed into barium carbonate and carbon monoxide.

At 300—400°, reactions occur similar to those observed by Vignon (A., 1911, ii, 391; 1914, i, 917) in his investigation of the action of carbon monoxide on lime, the corresponding equation being, (4) $2(H\cdot CO_2)_2Ba + BaO = 3BaCO_3 + CH_4$ or (5) $4(H\cdot CO_2)_2Ba + 2BaO = 6BaCO_3 + C_2H_4 + 2H_2$. That reaction (4) should take place at a higher temperature than (2) is indicated by thermochemical data, but

it could not be foreseen that above 400° the predominating reactions are (3) and the decomposition of the oxalate into carbonate and carbon monoxide. At temperatures exceeding 250°, carbon dioxide is formed in appreciable proportions; combination of reactions (2) and (3) evidently results in a change analogous to the formation of water gas from carbon monoxide and water vapour. T. H. P.

Action of Hydrazine Hydrate on Fats. PIETRO FALCIOLA and ANTONIO MANNINO (*Ann. Chim. Applicata*, 1914, **2**, 351—356).—Treatment of olive oil with hydrazine hydrate renders the oil turbid and raises its melting point considerably. The reaction proceeds in the cold and without appreciable development of heat, a slight ammoniacal odour being detectable in its early stages. The mass becomes whiter and the elevation of its melting point increases with the proportion of hydrazine hydrate employed. The solid substance separating from the oil is mostly soluble in hot alcohol, which deposits a crystalline substance, m. p. 110—112°. It is also soluble in acetone, which deposits a white substance, m. p. 65—67°. A number of other oils, both animal and vegetable, exhibit similar behaviour. Such hardened oils and fats either alone or in conjunction with other substances, such as naphthalene or anthracene, are suitable for the manufacture of candles.

Triolein behaves similarly with hydrazine hydrate, the resultant product, which contains C 74·32—74·47%, H 13·56—13·64% and N 9·03—9·07%, having m. p. 110—112°, about 76°, and 106—108° when crystallised from alcohol, acetone, and alcohol successively. The iodine number of the substance is 166, and vapours alkaline towards litmus are evolved when it is heated with potassium hydroxide.

The similar substance, m. p. 112—114°, obtained from fused tristearin has a still higher iodine number; its percentage composition is C 73·1, H 13·4 and N 9·1, and its molecular weight, determined in freezing benzene, varies from 178·8 to 320·4 as its concentration increases from 1·2% to 2·6%.

Tripalmitin and hydrazine hydrate yield a similar product, m. p. 108—109°. T. H. P.

Nitration of Mixed Dihalogenbenzenes. A. F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 846—849).—The author attempts to express quantitatively the directing influence of each of two substituents in a benzene nucleus on a third, entrant atom or group.

[With WIBAUT.]—When *o*-chlorotoluene is nitrated, the chlorine atom directs the nitro-group to positions 3 and 5, whilst the methyl group directs it to positions 4 and 6. If the proportion is determined (by solidification curves) in which *o*-chloro-4(and 6)-nitrotoluenes are present in regard to the isomerides, *o*-chloro-3 (and 5)-nitrotoluenes, the ratio, which is found to be Me : Cl = 1 : 1·475, is also the proportion of the substitution velocities caused by methyl and by chlorine.

[With VAN DEN AREND.]—The preceding ratio, applied to the case of the nitration of *p*-chlorotoluene, gives calculated quantities of the isomeric chloronitrotoluenes which agree approximately with those observed experimentally.

[In part, with HEINEKEN.]—The relative quantities of mononitrated chlorobromobenzenes produced by the nitration of *o*- or *p*-chlorobromobenzene are determined by estimating the amount of chlorine and bromine displaced by treatment with sodium methoxide; it is well known that only halogen atoms in the ortho- and para-positions to nitro-groups are eliminated by this reagent. Experiments on the nitration of *o*- and *p*-chlorobromobenzenes show that the ratio of the substitution velocities caused by chlorine and bromine when present together in the benzene nucleus is Cl : Br = 1 : 0·88. The ratio obtained in the case of *o*-chloroiodobenzene is Cl : I = 1 : 1·84. From these two ratios the authors calculate that the ratio for bromine and iodine should be Br : I = 1 : 2·30; the experimental value, obtained by the nitration of *o*-bromoiodobenzene, is Br : I = 1 : 1·75. C. S.

Action of Potassium Hydroxide on the Nitroamine of 4 : 6-Dinitro-3-methylanisidine. FRÉDÉRIC REVERDIN and ARMAND DE LUC (*Arch. Sci. phys. nat.*, 1914, [iv], **38**, 410—413).—The authors have determined the constitution of the substance, m. p. 182°, previously obtained by them (compare A., 1914, i, 831) by heating 4 : 6-dinitro-3-methylnitroaminoanisole with potassium hydroxide solution. This substance is now shown to be 4 : 6-*dinitro*-3-*methylaminophenol*, its constitution being proved by the fact that, on heating its silver salt emulsified in methyl alchol with methyl iodide on a water-bath for fifteen minutes, the methyl ether of 4 : 6-dinitro-3-methylaminophenol, m. p. 198° (compare Blanksma, *Rec. trav. chim.*, 1889, **8**, 276), is obtained. The original substance dissolves in nitric acid (D 1·52), giving a violet solution, turning to yellow on addition of water, and yielding by extraction with ether a *substance*, crystallising in small prisms, m. p. 173°. W. G.

The Three Fluorobenzoic Acids and their Nitration. J. H. SLOTHOUWER (*Rec. trav. chim.*, 1914, **33**, 324—342).—The author has prepared the three fluorobenzoic acids by oxidation of the corresponding fluorotoluenes with aqueous potassium permanganate. He has determined the solubility in water at 32°, and the electrical conductivity at 25° of these acids, and from them has prepared a number of derivatives.

o-Fluorobenzoic acid, m. p. 123°, gives a *chloride*, b. p. 206°, an *amide*, small, white needles, m. p. 116°, a *methyl* ester, b. p. 209°, an *ethyl* ester, b. p. 221°, and the following salts: *sodium* salt, $C_6H_4F\cdot CO_2Na$, *basic magnesium* salt, $C_6H_4F\cdot CO_2\cdot Mg\cdot OH,3H_2O$, *calcium* salt, $(C_6H_4F\cdot CO_2)_2Ca,2H_2O$, *barium* salt, $(C_6H_4F\cdot CO_2)_2Ba,H_2O$, *strontium* salt, $(C_6H_4F\cdot CO_2)_2Sr,2H_2O$, *zinc* salt, $(C_6H_4F\cdot CO_2)_2Zn,3H_2O$, *basic zinc* salt, $C_6H_4F\cdot CO_2\cdot Zn\cdot OH$, *cadmium* salt, $(C_6H_4F\cdot CO_2)_2Cd,H_2O$ and $2\frac{1}{2}H_2O$, *basic copper* salt, $C_6H_4F\cdot CO_2\cdot Cu\cdot OH$, *silver* salt, $C_6H_4F\cdot CO_2Ag$.

m-Fluorobenzoic acid, m. p. 123·6°, yields a *chloride*, b. p. 189°, an *amide*, white leaflets, m. p. 130°, a *methyl* ester, b. p. 197°, an *ethyl* ester, b. p. 209°, and the following salts: *sodium* salt, $C_6H_4F\cdot CO_2Na$,

potassium salt, $C_6H_4F\cdot CO_2K$, *calcium* salt, $(C_6H_4F\cdot CO_2)_2Ca,3H_2O$, *barium* salt, $(C_6H_4F\cdot CO_2)_2Ba,3H_2O$ and $4H_2O$, *cadmium* salt, $(C_6H_4F\cdot CO_2)_2Cd,2H_2O$, *basic copper* salt, $C_6H_4F\cdot CO_2\cdot Cu\cdot OH$, *silver* salt, $C_6H_4F\cdot CO_2Ag$.

p-Fluorobenzoic acid, m. p. 182°, gives a *chloride*, b. p. 193°, an *amide*, white leaflets, m. p. 154·5°, a *methyl* ester, b. p. 198°, an *ethyl* ester, b. p. 210°, m. p. 26°, and the following salts: *sodium* salt, $C_6H_4F\cdot CO_2Na$, *calcium* salt, $(C_6H_4F\cdot CO_2)_2Ca,3H_2O$, *barium* salt, $(C_6H_4F\cdot CO_2)_2Ba$, and with $2H_2O$ and $4H_2O$, *zinc* salt, $(C_6H_4F\cdot CO_2)_2Zn,3H_2O$, *cadmium* salt, $(C_6H_4F\cdot CO_2)_2Cd,4H_2O$, *basic lead* salt, $C_6H_4F\cdot CO_2\cdot Pb\cdot OH,3H_2O$, *copper* salt, $(C_6H_4F\cdot CO_2)_2Cu$, *silver* salt, $C_6H_4F\cdot CO_2Ag$.

o-Fluorobenzoic acid is readily nitrated when slowly added to nitric acid (D 1·52) at 0°. The two isomeric nitro-compounds formed are separated by fractional crystallisation of their potassium salts from water, the salts being then decomposed with dilute hydrochloric acid. The main product is *2-fluoro-5-nitrobenzoic acid*, m. p. 138—139°, which is almost white and gives a *potassium* salt crystallising in long needles. Its constitution was proved by heating it with alcoholic ammonia in a sealed tube at 130—140°, the product being 5-nitro-2-aminobenzoic acid, m. p. 265° (compare Hübner, A., 1878, 148). The other product of the nitration, only present as a trace, was *2-fluoro-3-nitrobenzoic acid*, m. p. 160°.

m-Fluorobenzoic acid, is nitrated under similar conditions, giving *3-fluoro-6-nitrobenzoic acid*, m. p. 134·5°, which is converted by alcoholic ammonia into 6-nitro-3-aminobenzoic acid (compare Griess, *Ber.*, 1872, **5**, 198). A certain amount of resinous products are formed during this nitration.

p-Fluorobenzoic acid is nitrated by adding it slowly to boiling nitric acid (D 1·52) and pouring the product into excess of cold water. The sole product is *4-fluoro-3-nitrobenzoic acid*, slender needles, m. p. 121—122°, which, with alcoholic ammonia, yields 3-nitro-4-aminobenzoic acid (compare Salkowski, this Journ., 1875, 72).

Comparing the four series of fluoronitro-, chloronitro-, and bromonitrobenzoic acids, they show in each case a steady rise in the m. p. on passing from the fluoro- through the chloro- to the bromo-derivatives.

The point of entrance of the nitro-group in all the above nitrations is, in every case, what would be expected from a knowledge of the behaviour of fluorobenzene and benzoic acid respectively on nitration.

W. G.

Preparation of Halogen-alkyl Esters of *o*-Acetoxybenzoic Acid. R. Wolffenstein (D.R.-P. 276809; from *J. Soc. Chem. Ind.*, 1914, **33**, 1172. Compare A., 1912, i, 556).—Polyhaloidalkyl esters of salicylic acid are treated with acetylating agents. For example, *tert.*-trichlorobutyl salicylate is heated with acetic anhydride and anhydrous sodium acetate at 160—180°, and the product is treated with water and with aqueous sodium carbonate, the ester being finally extracted by ether.

C. S.

Preparation of Halogen-alkyl Esters of *o*-Acyloxybenzoic Acids. R. WOLFFENSTEIN (D.R.-P. 276810; from *J. Soc. Chem. Ind.*, 1914, **33**, 1172. Compare preceding abstract).—Polyhalogen-alkyl esters of salicylic acid are treated with acylating agents other than those which introduce the acetyl group. C. S.

***cis*-Caronic Acid and Some of Its Derivatives.** R. LOCQUIN (*Bull. Soc. chim.*, 1914, [iv], **15**, 747—751. Compare Baeyer and Ipatiev, A., 1897, i, 83; and Perkin and Thorpe, T., 1899, **75**, 48).—*cis*-Caronic acid can readily be distinguished from its isomeride terebic acid, by its instantaneous m. p., taken on mercury, that of the former rising to 186°, and that of the latter remaining at 174°. *Methyl* cis-*caronate*, $C_9H_{14}O_4$, is a colourless, mobile liquid, b. p. 111—112°/14 mm. *Ethyl* cis-*caronate*, $C_{11}H_{18}O_4$, has b. p. 129—130°/13 mm. The acid can be readily regenerated from the esters by boiling with 15% aqueous hydrochloric acid under reflux until the oily layer disappears. Caronic anhydride is best prepared by boiling the *cis*-acid for some time with an excess of acetyl chloride or thionyl chloride. In benzene solution with aniline, it yields an *acid anilide*,

$$CO_2H\cdot C_5H_8\cdot CO\cdot NHPh,$$

m. p. 205°, which, if kept for some time at 180—190°, is converted into the *anil*, $C_5H_8\langle\begin{matrix}CO\\CO\end{matrix}\rangle NPh$, m. p. 143°. W. G.

Glucosides of Chalkones [Phenyl Styryl Ketones]. G. BARGELLINI (*Gazzetta*, 1914, **44**, ii, 520—528).—The author has prepared various glucosides of phenyl styryl ketones by condensation of the glucoside of salicylaldehyde, helicin, and of the glucoside of vanillin with different hydroxy-ketones. The condensations take place in alcoholic solution at the ordinary temperature and in presence of either 40% sodium hydroxide solution or piperidine. The glucosides are not resolved into their constituents by emulsin and therefore belong to the *a*-series. They are not hydrolysed by acids, but they dissolve in concentrated sulphuric acid, giving first an intense red coloration and afterwards an orange-yellow or red solution.

The *glucoside* of 4-*hydroxyphenyl* 2-*hydroxystyryl ketone*,

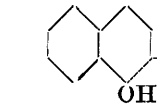
$$OH\cdot C_6H_4\cdot CO\cdot CH{:}CH\cdot C_6H_4\cdot O\cdot C_6H_{11}O_5,$$

prepared from the glucoside of salicylaldehyde and *p*-hydroxyacetophenone, forms a felted mass of minute, cream-yellow needles, m. p. 257—259° (decomp.).

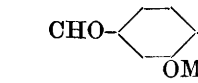
The *glucoside* of 2-*hydroxy*-4-*methoxyphenyl* 2-*hydroxystyryl ketone*, $OMe\cdot C_6H_3(OH)\cdot CO\cdot CH{:}CH\cdot C_6H_4\cdot O\cdot C_6H_{11}O_5$, obtained from the glucoside of salicylaldehyde and 2-hydroxy-4-methoxyacetophenone, forms flocks of canary-yellow needles, m. p. 213—215°.

The *glucoside* of 2-*hydroxy*-5-*methoxyphenyl* 2-*hydroxystyryl ketone*, $C_{22}H_{24}O_9$, forms small, orange-yellow needles, m. p. 255—227°.

The *glucoside* of 2-*hydroxy*-3 : 4-*dimethoxyphenyl* 2-*hydroxystyryl ketone*, $OH\cdot C_6H_2(OMe)_2\cdot CO\cdot CH{:}CH\cdot C_6H_4\cdot O\cdot C_6H_{11}O_5$, forms bright yellow needles, m. p. 195—196° (decomp.).



The *glucoside* of 1-*hydroxy*-2-*naphthyl* 2-*hydroxystyryl ketone* (annexed formula), prepared from 2-acetyl-α-naphthol and the glucoside of salicylaldehyde, forms flocculent aggregates of minute, orange-red needles, m. p. 244—246° (decomp.).



Tetra-acetylglucovanillin (annexed formula), prepared from tetra-acetylbromoglucose and vanillin in presence of sodium hydroxide, forms shining, colourless prisms, m. p. 143—144°.

The *glucoside* of 2-*hydroxy*-4-*methoxyphenyl* 4-*hydroxy*-3-*methoxystyryl ketone*, $OMe\cdot C_6H_3(OH)\cdot CO\cdot CH{:}CH\cdot C_6H_3(OMe)\cdot O\cdot C_6H_{11}O_5$, prepared from the preceding compound and 2-hydroxy-4-methoxyacetophenone, forms canary-yellow crystals, m. p. 220—225°. T. H. P.

Preparation of Anthraquinone. Chemische Fabrik Griesheim-Elektron (U.S. Pat. 1119546; from *J. Soc. Chem. Ind.*, 1915, **34**, 22).—Anthracene is treated with nitric acid in the presence of a mercury salt and an indifferent liquid below 60°. The product, which is a mixture of unstable *meso*-nitro-derivatives of anthracene, is converted into anthraquinone by treatment with an oxidising agent, in the presence of a mercury salt, above 60°. C. S.

Preparation of Aminoanthraquinones. Farbwerke vorm. Meister, Lucius, & Brüning (Fr. Pat. 469741; from *J. Soc. Chem. Ind.*, 1915, **34**, 22. Compare this vol., i, 20).—Organic amino-compounds may be used in place of ammonia. C. S.

Constituents of Essential Oils. I. Galbanum Oil. II. Syntheses in the Sesquiterpene and the Diterpene Series. F. W. Semmler and K. G. Jonas (*Ber.*, 1914, **47**, 2068—2082).—I. The oil obtained by the distillation of Galbanum resin has b. p. 55—195°/15 mm., D^{25} 0·9353, n_D^{25} 1·49395, and α_D^{25} +8°. By repeated fractional distillation, it is separated into nine fractions, of which the following have been examined. The fraction, b. p. 56·5—75°/15 mm., obtained in 29·5% yield, contains pinene, nopinene (β-pinene), and myrcene, but no camphene.

The fraction, b. p. 100—120°/15 mm. (2·5%), contains a *substance*, $C_{10}H_{16}O$ (enolisible ketone?), which can be esterified and yields by oxidation a ketonic acid, $C_{10}H_{16}O_3$; from the latter, the dicarboxylic *acid*, $C_9H_{14}O_4$, is obtained by the action of an alkaline solution of bromine.

The fractions, b. p. 120—150°/15 mm. (5%), contain cadinene.

The fractions, b. p. 150—170°/15 mm. (36%), contain a tertiary sesquiterpene alcohol, *cadinol*, $C_{15}H_{26}O$, which in a slightly impure state has b. p. 155—165°/15 mm., D^{20} 0·9720, n_D 1·50702, and α_D +22°, and yields an *acetate*, $C_{17}H_{28}O_2$, b. p. 160—170°/9 mm., D^{19} 0·9916, n_D^{19} 1·49870, and α_D^{19} +14°. By treatment with potassium hydrogen sulphate, phthalic or succinic anhydride, or formic acid,

cadinol is converted into *l*-cadinene. By reduction with hydrogen in the presence of platinum, *l*-cadinene is converted into *l-tetrahydrocadinene*, $C_{15}H_{28}$, b. p. 125—128°/10 mm., $D^{20\cdot5}$ 0·8838, $n_D^{20\cdot5}$ 1·48045, $\alpha_D^{20\cdot5} - 20°$. *l*-Tetrahydrocadinene, obtained by the reduction of *l*-cadinene dihydrochloride by sodium and alcohol, has b. p. 125—128°/10 mm., $D^{21\cdot5}$ 0·8827, $n_D^{21\cdot5}$ 1·48094, and $\alpha_D^{21\cdot5} - 52°$. The colour reactions of cadinene, described by Wallach, could not be obtained by the authors.

II. Octahydro-α-camphorene (Semmler and Rosenberg, A., 1913, i, 377) has b. p. 183—186°/14 mm., D^{20} 0·8331, n_D 1·46001, and $[\alpha]_D \pm 0°$.

From the liquid products obtained by the action of hydrogen chloride on the diterpene fraction of polymerised myrcene, there is produced by the elimination of hydrogen chloride, a bicyclic diterpene, $C_{20}H_{32}$, for which the name iso-*α-camphorene* is proposed. It has b. p. 193—197°/19 mm., D^{21} 0·9029, n_D 1·50300, and $[\alpha]_D \pm 0°$, and is reduced by hydrogen and platinum to *hexahydro*iso-*α-camphorene*, $C_{20}H_{38}$, b. p. 180—186°/14 mm., D^{21} 0·8588, n_D 1·46800, and $[\alpha]_D \pm 0°$.

By heating with anhydrous oxalic acid in a sealed tube, linalool has been converted directly into α-camphorene, and citronellaldehyde into a *diterpene oxide*, $C_{20}H_{34}O$, b. p. 190—200°/17 mm., D^{20} 0·9193, n_D 1·49156, $\alpha_D + 4°$, which is reduced by hydrogen and platinum to a saturated *substance*, $C_{20}H_{38}O$, b. p. 183—187°/17 mm., D^{20} 0·8944, n_D 1·47319, $\alpha_D + 3°$.

By reduction in dry ether by hydrogen and platinum, *cyclo*isoprenemyrcene (Semmler and Jonas, A., 1913, i, 742) yields *hexahydrocyclo-isoprenemyrcene*, $C_{15}H_{30}$, b. p. 133—135°/15 mm., D^{20} 0·8245, n_D 1·45497, $\alpha_D \pm 0°$, the formation of which is a complete proof of the monocyclic nature of *cyclo*isoprenemyrcene.

Since cadinene has a bicyclic structure of the naphthalene type, and since the condensation of acyclic terpenes with isoprene yields monocyclic sesquiterpenes, the authors hoped to synthesise bicyclic sesquiterpenes, for example, cadinene, by condensing monocyclic terpenes with isoprene. By heating *l*-α-phellandrene with isoprene in a sealed tube, a *sesquiterpene*, $C_{15}H_{24}$, is obtained, which has b. p. 129—132°/15 mm., D^{20} 0·8976, n_D 1·4949, and $\alpha_D - 15°$, and is probably identical with β-santalene. Limonene and isoprene do not react by heating in a sealed tube, but by their reaction in glacial acetic acid at 35°, or by treating the two hydrocarbons, in the proportion 2 : 1, with about three times the quantity of ethylsulphuric acid at $-18°$ to $-10°$, a *sesquiterpene*, $C_{15}H_{24}$, b. p. 120—127°/10 mm., D^{20} 0·889, n_D 1·502, $\alpha_D \pm 0°$, is obtained, which appears to be monocyclic. Similar results (and probably the same sesquiterpene) are obtained with isoprene and pinene or sabinene. C. S.

The Synthesis of Colouring Matters. E. Noelting (*Arch. Sci. phys. nat.*, 1914, [iv], **38**, 244—262, 337—343).—An historical survey of the chemistry of dyes, containing a classification of those used on a large scale into groups, a brief account of the properties of each group being given. W. G.

Vat [Anthracene] Dyes and Intermediate Products for Use in their Preparation. BADISCHE ANILIN- & SODA-FABRIK (1st. Add. to Fr. Pat. 458949 ; from *J. Soc. Chem. Ind.*, 1915, **34**, 22).—Imines of anthracene-1 : 9-dicarboxylic acid, in which the hydrogen of the imino-group is replaced by a hydroxyl, alkyl, or aryl group, are obtained by treating the acid or its anhydride with hydroxylamine or with an aliphatic or aromatic primary amine. For example, the methylimine is obtained by heating anthracene-1 : 9-dicarboxylic anhydride with ten times its weight of 13% aqueous methylamine at 150° for 5 hours.

The substituted imines are converted into vat dyes, analogous to those obtained according to the principal patent, by fusion with alkalis. The dyes may also be obtained by treating the dyes mentioned in the principal patent with alkylating or arylating agents. In general, the products dye rather bluer shades than do the substances from which they are derived. C. S.

Preparation of an Oxidation Product of Isatin. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 276808 ; from *J. Soc. Chem. Ind.*, 1914, **33**, 1151).—Isatin is oxidised by potassium permanganate in neutral aqueous suspension, yielding a *compound*, $C_{16}H_8O_2N_2$, m. p. 262°, yellow crystals, which is converted into indigo-white by sodium hyposulphite and an excess of alkali hydroxide, and is very reactive and therefore suitable for the preparation of indigoid dyes. C. S.

Diketomethyltriazine and its Derivatives. A. OSTROGOVICH (*Gazzetta*, 1914, **44**, ii, 562—585).—4:6-Diketo-2-methyl-1:3:5-triazine (compare A., 1911, i, 1036) may be conveniently prepared by heating biuret with acetyl chloride in a sealed tube, the isolation and purification of the acetylbiuret being thus avoided. The free base crystallises either in the anhydrous state or with $1H_2O$, and has m. p. 276—277° (decomp.). The marked acidity of the compound, shown by the ability of its aqueous solution to decompose carbonates, and the fact that all its metallic derivatives contain only one equivalent of metal, are in better accord with the enolic structure $NH<\begin{matrix}CMe{:}N\\CO{-}{-}N\end{matrix}>C{\cdot}OH$ than with the diketonic formula previously given.

The *hydrochloride*, $C_4H_5O_2N_3,HCl$, was prepared, but the corresponding sulphate and selenate could not be obtained, the *hydrogen sulphate*, $C_4H_5O_2N_3,H_2SO_4$ (or $+H_2O$), and *hydrogen selenate*,

$$C_4H_5O_2N_3,H_2SeO_4,\tfrac{1}{2}H_2O,$$

being formed under all the conditions employed. When heated at above 100° or when repeatedly evaporated in aqueous solution on a water-bath, the platinichloride, $(C_4H_5O_2N_3)_2,H_2PtCl_6,4H_2O$ (compare Nencki, *Ber.*, 1876, **9**, 234), loses hydrogen chloride with formation of *dichloroplatodiketomethyltriazine*, $C_4H_4O_2N_3{\cdot}PtCl_2{\cdot}C_4H_4O_2N_3$, which separates as a pale yellow powder.

Attempts to prepare the aurichloride resulted in the reduction of the auric chloride to metallic gold, which was deposited in shining leaflets. This reaction is very sensitive and may be employed to detect small quantities of the base, either in the pure state or in

admixture with a large proportion of acetylbiuret, which does not reduce auric chloride.

Diketomethyltriazine phosphomolybdate forms minute, lemon-yellow, acicular prisms.

The *sodium* derivative of diketomethyltriazine, $C_4H_4ON_3 \cdot ONa$, crystallises with $1\frac{1}{2}H_2O$ or $2H_2O$. The silver, $+\frac{1}{2}H_2O$ and $+H_2O$, the *barium*, $+7H_2O$, and the *basic lead* derivatives,

$$O(\cdot Pb \cdot C_4H_4O_2N_3)_2 + 8H_2O,$$

were prepared. T. H. P.

Mechanism of Formation of Azo-compounds by the Action of Diazonium Salts on Phenols and on Amines. G. CHARRIER (*Gazzetta*, 1914, **44**, ii, 503—516).—The author discusses the various theories which have been advanced to explain the formation of hydroxy- and amino-azo-compounds by the action of diazonium salts on phenols and on amines. None of these theories explains, however, the varying reactivity in this respect shown by diazonium salts of phenols and of their ethers. The most secure basis for any explanation of the mechanism of this combination is furnished by the very general diazo-decomposition of the nitrates of (1) hydroxyazo-compounds and of their ethers, and (2) aminoazo-compounds and of their alkyl derivatives (compare Charrier and Ferreri, A., 1912, i, 812; 1913, i, 535, 1111, 1112, 1113; 1914, i, 597, 599, 748, 1178). One advantage of such an explanation is that it allows of the reconciliation of Blomstrand's structural formulæ for diazonium salts with certain of their more important reactions, such as the formation of hydroxy- and amino-azo-compounds. In the light of the author's experimental results, it is probable that the formation of the so-called diazoamino-compounds or aryldiazoanilides, to which the nitrates of hydroxyazo-compounds show certain analogies in behaviour, may be regarded as taking place according to the scheme:

$$Ar \cdot NH_2 + N{:}NAr'Cl = \overset{H}{\overset{/}{N}}HAr \cdots N{:}NAr'Cl = NHAr \cdot N{:}NHAr'Cl =$$
$$= NHAr \cdot N{:}NAr' + HCl.$$

T. H. P.

The Coagulation of Albumin by Pressure. P. W. BRIDGMAN (*J. Biol. Chem.*, 1914, **19**, 511—512).—Egg-albumin was enclosed in a nickel-steel case, and pressure transmitted to it by mercury. If the pressure is applied slowly, any rise of temperature is negligible; a pressure of 5000 atmospheres for thirty minutes rendered the white of egg a little stiff; 6000 produced coagulation like curded milk; 7000 made it like a hard-boiled egg. The rate of coagulation is increased at low temperatures. W. D. H.

The Preparation of Hæmatin. J. A. MENZIES (*Proc. physiol. Soc.*, 1914; *J. Physiol.*, **49**, iv—v).—The blood is mixed with a quarter of its volume of a syrupy solution of potassium carbonate, and heated on the water-bath until it sets into a brown coagulum. This is thrown into twice its volume of alcohol, and left overnight for thorough extraction of the hæmatin; on neutralising this dark brown extract with hydrochloric acid, hæmatin is precipitated, and is

purified by washing with distilled water, alcohol, and ether. Hæmatin may also be precipitated by ether or by calcium chloride and ammonia, or baryta mixture. Calcium and barium compounds respectively are thus obtained. W. D. H.

Hæmatin Compounds. J. A. MENZIES (*Proc. physiol. Soc.*, 1914; *J. Physiol.*, **49**, v—vi).—Hæmatin exists in two forms: one which occurs in solutions and moist precipitates, is soluble in dilute hydrochloric acid. The other, the dry substance, is insoluble in dilute acid, but is readily soluble in alkali. The first may be a hydrated substance, and is changed by drying in the same way that a lactone is formed from a hydroxy-acid.

Hæmatin in acid solution is precipitated by dialysis, the acid acting as a solvent, and not forming a compound. In alkaline solution, it is not precipitated on dialysis, although the solution becomes neutral to litmus. Sodium and potassium therefore form compounds with hæmatin which are soluble in water. The calcium and barium compounds are insoluble in water, but dissolve in alkali with the formation of the alkali compound. Hæmoglobin is analogous to a salt, globin playing the part of a base, and hæmatin that of an acid. W. D. H.

Physiological Chemistry.

The Respiratory Exchange in Fresh-water Fish. II. Brown Trout. JOHN ADDYMAN GARDNER and CONSTANCE LEETHAM (*Biochem. J.*, 1914, **8**, 591—597. Compare A., 1914, i, 1149).—Brown trout are asphyxiated by water the oxygen content of which is sufficient to keep roach alive. If the water is saturated with oxygen, the consumption of oxygen by trout is doubled by a rise of 10°. Hence they pump more water through their gills at the higher temperature. The extra work done in respiration is a factor which has to be also taken into account. W. D. H.

The Solubility of Oxygen in the Serum of Limulus polyphemus, L., and in Solutions of Pure Limulus Hæmocyanin. CARL L. ALSBERG and WILLIAM MANSFELD CLARK (*J. Biol. Chem.*, 1914, **19**, 503—510).—The serum of *Limulus* under diminished pressure sets free about as much oxygen as distilled water or sea water under similar conditions. A 10% solution of hæmocyanin, which contains about three times as much hæmocyanin as the serum, liberates about 20% more. This increase is too slight to warrant the assumption that hæmocyanin is an oxygen carrier. This contrasts with the results of Henze on Octopus blood. The Limulus hæmocyanin may, however, be more efficient in this direction than the gas analyses reveal, since its combination with oxygen does not dissociate appreciably at low pressures. With the aid of

the copper of the pigment, oxygen may perhaps be catalytically transferred to the tissues within the body. W. D. H.

The Water Content of the Blood. E. F. TERROINE (*Bull. Soc. chim.*, 1914, [iv], **15**, 752; from *Compt. rend. Soc. Biol.*, 1914, **76**, 523).—The normal organism in the case of the dog maintains its water content of the blood constant, variations of 5% being exceptional. The digestive processes have but very slight influence on the hydremic constant. On the other hand, during inanition, the water content of the blood varies, the direction of these variations being different in different animals. W. G.

Inactivation of Complement by Shaking. HANS SCHMIDT (*J. Hygiene*, 1914, **14**, 417—436).—Shaking produces alterations of the physical conditions in the serum, which account for the loss of complementing power it undergoes. The conception that the complement is a ferment is unnecessary, although it is admitted that this is not yet fully proved. W. D. H.

Berkefeld Filtration of Complement. HANS SCHMIDT (*J. Hygiene*, 1914, **14**, 437—452).—In the Berkefeld filtration of fresh guinea-pig serum, adsorption on the filter surface takes place, and the serum passes unaltered if the saturation of the adsorbing surface has become complete. The adsorption involves, most probably, the albumins first; this, secondarily, influences the filtrability of the globulins. The physical conditions of the serum, as regards salt concentration and dilution, as well as hydrogen-ion concentration, modify the effect of filtration to a great extent. W. D. H.

Influence of Polyhydric Phenols and Phenolcarboxylic Acids on the Diastatic Hydrolysis of Albuminoids by Pepsin in Presence of Acid. LUIS GUGLIALMELLI (*Anal. Soc. Quim. Argentina*, 1914, **2**, 186—195).—A study of the inhibitory action exerted by phenol, dihydric and trihydric phenols, and salicylic, gallic, and tannic acids on the process of digestion. The extent of the influence is conditioned, not only by the nature of the substituents attached to the nucleus, but also by their relative position. A. J. W.

The Metabolism of the Salivary Gland. I. The Nitrogen Metabolism of the Resting Gland. C. G. L. WOLF and J. BARCROFT (*J. Physiol.*, 1914, **49**, 95—108).—In five out of eight experiments on the dog's submaxillary gland, the gland took more non-protein nitrogen from the blood than it contributed to it; in one there was equilibrium, and in the remaining two there was a balance towards the blood. The maximal amount taken up was 0·18 mg. of nitrogen per gram of gland per minute. In three of six experiments no urea-exchange occurred; in one the blood, and in two the gland, acquired urea; the maximum urea-exchange was 0·014 mg. per gram of gland per minute; the main exchange is therefore in "residual nitrogen." The maximal differ-

ence in composition between the arterial and venous bloods in non-protein nitrogen was 5·5 ± 0·8 mg. per 100 c.c. of blood.

W. D. H.

Fatty Acid Metabolism in the Liver. III. Fatty Acid Infiltration of the Liver During Pregnancy and Lactation. R. Coope and V. H. Mottram (*J. Physiol.*, 1914, **49**, 23—33. Compare A., 1910, ii, 525).—In cats without previous dieting, fatty infiltration of the liver was found in both pregnant and non-pregnant animals. In rabbits kept on an ample diet, a decided increase in the fat of the liver occurred at or about the time of parturition. This confirms the view that the change is physiological rather than pathological. W. D. H.

Endogenous Uric Acid Metabolism. G. W. Raiziss, H. Dubin, and A. I. Ringer (*J. Biol. Chem.*, 1914, **19**, 473—485).—On a meat-free diet, the output of uric acid in ten people was found to be much lower than previously accepted; during rest, this remained nearly constant per diem. It is raised by work or protein food. In changing diets, at least a week must elapse before the true value of the output becomes constant. If the diet is also nuclein-free, the output drops to half of what occurs on a vegetable diet (0·04 gram per day). The small values render the investigation of endogenous uric acid metabolism very difficult. W. D. H.

The Influence of the Vagus on Pancreatic Secretion. G. von Aurep (*J. Physiol.*, 1914, **49**, 1—9).—Evidence is adduced that apart from the action of the chemical stimulus, the vagus nerve contains secretory fibres (paralysed by atropine) which affect the pancreas. In these experiments, any entrance of acid chyme into the duodenum was prevented by ligaturing the pylorus. There are also secreto-inhibitory fibres. The secretion of the juice provoked by secretin is stopped by stimulation of the vagus. Both sorts of fibres are equally distributed in all branches of the nerve. The latent period is always a long one, and sometimes no secretion appears until after several stimulations have been applied, and even then the effect is a small one compared with that produced by secretion; and the experiment of stimulating the vagus always fails to produce any secretion at all unless the spinal cord has been divided without injury to the bulb. W. D. H.

The Existence of Philothion in the Lens of the Eyes of Animals. J. de Rey-Pailhade (*Compt. rend.*, 1915, **160**, 37—38).—The author has shown philothion to be present in the lens of the eyes of cows, calves, sheep, horses, pigs, rabbits, of a cephalopod, *Octopus vulgaris*, and in the lens of his own left eye, operated on eight months previously for cataract. This fact places the tissue of the lens in the same category with striated muscle. W. G.

The Action of Poisons on Reductase and Attempts to Isolate the Enzyme. David Fraser Harris and Henry Jermain Maude Creighton (*Biochem. J.*, 1914, **8**, 585—590).—The reductase

of pigeon's liver and muscle is soluble to some extent in normal saline solution, and in a mixture of normal saline and glycerol, but not in pure glycerol. All attempts to isolate the enzyme failed. The poisonous action on the enzyme of ten substances, chosen at random, was investigated. W. D. H.

The Distribution of Arsenic in a Human Body. FRANK P. UNDERHILL (*J. Biol. Chem.*, 1914, **19**, 513).—The body was exhumed three months after death in a medico-legal case. A table is given of the amount of arsenic in the various organs. A new feature brought out is that significant quantities were obtained from the brain and spinal cord. The case was one of chronic poisoning. W. D. H.

The Presence of So-called "Complement" in Milk. R. TANNER HEWLETT and CECIL REVIS (*J. Hygiene*, 1914, **14**, 481—497). —Milk always contains a "complementary substance." This is specially abundant in colostral and mastitis milks; in the latter, amboceptor may be present as well. No relation between the amount of complementary substance and cellular elements in the milk could be traced. This hæmolytic system is of great delicacy. The true nature of milk "complement" is doubtful. W. D. H.

The Excretion of Creatinine in Man on a Prolonged Creatine-free Diet. A. I. RINGER and G. W. RAIZISS (*J. Biol. Chem.*, 1914, **19**, 487—492).—In four people kept on prolonged creatine- and creatinine-free diet, the excretion of creatinine dropped 10 or 22%. Tables of the daily output are appended. W. D. H.

The Isolation of *p*-Hydroxyphenylacetic Acid from the Urine in Disease. N. MUTCH (*Proc. physiol. Soc.*, 1914; *J. Physiol.*, **49**, ii—iii).—In diseases of the alimentary tract where there is delay in the passage of food, hydrophenolic substances were detected in the urine (seventy cases) by applying Millon's test to an ethereal extract of acidified urine. Normal urine gives no such reaction. In one case, *p*-hydroxyphenylacetic acid was separated from the urine. Six litres were acidified with sulphuric acid and extracted with ether. The extract was evaporated at room temperature, and the residue extracted with chloroform, which was also slowly evaporated. The residue was dissolved in 5% sodium carbonate, filtered, acidified, refiltered, and extracted with ether. The ether was evaporated as before, and hippuric acid removed by cold benzene, to which a little chloroform had been added. The final residue was repeatedly recrystallised from boiling benzene, and found to consist of flat needles, melting at 148°, and when mixed with synthetic *p*-hydroxyphenylacetic acid, at 148·5°. The excreted acid doubtless arises from tyrosine in the intestine, an intermediate stage produced by bacteria being *p*-hydroxyphenyl-ethylamine. W. D. H.

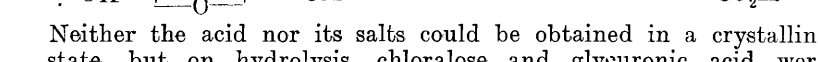
The Respiratory Exchanges of the Heart in the Diabetic Animal. E. H. STARLING and C. L. EVANS (*J. Physiol.*, 1914, **49**, 67—88).—Experiments with the heart-lung preparation show that the normal dog's heart uses 3·2 c.c. of oxygen per gram when doing moderate work, and the respiratory quotient is 0·85. It is calculated that, on a mixed diet, the heart uses about 1·6 mg. of carbohydrate per gram per hour; the lung uses not more than 0·5 mg. of sugar per hour. The respiratory quotient of the heart in pancreatic diabetes is 0·71, and this is not raised by the addition of dextrose, or in the acceleration produced by adrenaline. This indicates a depression of the utilisation of carbohydrate by diabetic tissue, but there are also other modifications of tissue metabolism which might mask moderate carbohydrate consumption. The oxygen usage by the diabetic heart is the same as in the normal state. The normal heart does not alter its metabolism when fed with diabetic blood; the diabetic heart is also unchanged when fed on normal blood. Acid extracts of pancreas act on the normal heart like adrenaline. The effects on the diabetic heart are similar, but prolonged rises of the respiratory quotient have been obtained.

W. D. H.

Liver Nitrogen in Anaphylaxis. GEORGE BARGER and HENRY HALLETT DALE (*Biochem. J.*, 1914, **8**, 670—679).—The statement of Hashimoto and Pick (A., 1914, i, 769) that the liver and spleen in anaphylaxis contain excess of non-coagulable nitrogen appeared to be rich in promise for further work. The authors' desire to work along these lines has, however, been frustrated by a complete failure to corroborate the findings of Hashimoto and Pick.

W. D. H.

The Destiny of Chloralose in the Organism and its Relationships with the Glycuronic Conjugation. M. TIFFENEAU (*Compt. rend.*, 1915, **160**, 38—41).—The administration of chloralose to a dog, either by way of the œsophagus or by injection into the peritoneum, results in an elimination of a portion of this substance unchanged in the urine. At the same time, there is excreted in the urine another organic chloro-derivative, which has been shown to be a *chloralose-glycuronic acid*, having the constitution



Neither the acid nor its salts could be obtained in a crystalline state, but on hydrolysis, chloralose and glycuronic acid were isolated as the only products. From urine this compound is not precipitated by normal lead acetate, but almost entirely by ammoniacal lead acetate. The formation of this compound does not support the hypothesis of Sundwick and Fischer on the mechanism of the glycuronic conjugation, since, according to their views, chloral and trichloroethanol should have been amongst the products of hydrolysis. Chloralose does not decompose in the

animal organism into chloral and dextrose, but the physiological effects produced by its administration are due to the chloralose as such, and not to any liberated chloral. W. G.

Behaviour of Ethylurethane, Piperonaldehyde, and Piperonylidenebisurethane in the Organism. G. BIANCHI (*Boll. Chim. Farm.*, 1914, **53**, 324—335).—One thousand grams of water dissolve 0·0649 gram of piperonylidenebisurethane (compare A., 1913, i, 482) at 11·5° and 0·762 gram at 100°. Owing, perhaps, to its slight solubility, this compound exhibits little physiological activity, and functions as a mild hypnotic, capable of producing sound, although not too deep, sleep, but not of depressing the cardiac or respiratory functions. This action is partly due to the slow absorption of small proportions of nascent ethylurethane, gradually liberated, together with piperonaldehyde, in the organism; the aldehyde may possibly intensify the hypnosis, but has no further appreciable effect. Administration of piperonylidenebisurethane occasions also the formation of an excessive proportion of carbamide and the biochemical synthesis of two conjugated glycuronic acids, one from the ethylurethane and the other from the piperonaldehyde.

T. H. P.

Chemistry of Vegetable Physiology and Agriculture.

Protective Action, against Magnesium Carbonate, of Calcium Carbonate for Azotobacter chroococcum. CHAS. B. LIPMAN and PAUL S. BURGESS (*J. Agric. Sci.*, 1915, **6**, 484—498).—In mannitol solution cultures of *A. chroococcum*, calcium carbonate acts only as a stimulant, and is not toxic in concentrations of 2%. Magnesium carbonate, under similar conditions, is toxic in concentrations in excess of 0·1—0·2%.

In soil cultures, calcium carbonate, up to 1·4% of the dry weight of the soil, has no effect; higher amounts have a slightly toxic effect in a sandy soil. In this soil, nitrogen fixation is almost completely inhibited by 0·1% of magnesium carbonate; this is due to the magnesium, and not to its alkalinity, which is beneficial.

In solution and in soil cultures, calcium carbonate has a protective action against the toxic effect of magnesium carbonate. In solutions, the best ratio is $CaCO_3/MgCO_3 = 6 : 1$, when the absolute values are 0·2% and 1·25%, respectively, of magnesium and calcium carbonates. In soil cultures, the best ratio seems to be 15 : 1 when 0·1% of magnesium carbonate is present. N. H. J. M.

Organic Chemistry.

A Method of Determining the Constitution of the Monoglycerophosphoric Esters, and the Constitution of Crystalline Sodium Glycerophosphate. L. GRIMBERT and O. BAILLY (*Compt. rend.*, 1915, **160**, 207—210; compare Carré, A., 1912, i, 155; Paolini, A., 1912, i, 826).—The authors have devised a chemical method of determining whether sodium glycerophosphate and monoglycerophosphoric esters in general are α-esters (formula I.) or β-esters (formula II.),

$PO(ONa)_2\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$ (I.) $\qquad PO(ONa)_2\cdot O\cdot CH(CH_2\cdot OH)_2$ (II.)

An α-ester, on oxidation in the absence of all hydrolysis, should give a compound of the type $R\cdot CO\cdot CH_2\cdot OH$, which can be characterised by Denigès's reactions (compare A., 1909, ii, 272, 273, 353). This test has been applied to the crystalline sodium glycerophosphate obtained by Poulenc's method, and to the uncrystallisable salt obtained at the same time. The oxidising agent used was bromine water, containing 0·25% bromine, the oxidation being effected in the cold to avoid any hydrolysis by the nascent hydrogen bromide. The oxidation product from the crystalline salt gave neither of the Denigès's reactions, whilst that from the uncrystallisable salt gave both the reactions. Crystalline sodium glycerophosphate,

$$PO_4Na_2\cdot C_3H_5(OH)_2,5H_2O,$$

is therefore a salt of the β-acid and its constitution is represented by formula II. W. G.

The Preparation of Some Esters. F. BODROUX (*Compt. rend.*, 1915, **160**, 204—207).—On slowly distilling a mixture of formic acid, ethyl alcohols, and water, ethyl formate was obtained, the yield of the ester diminishing as the amount of water present was increased. Attempts were made to use formic acid as catalyst in the esterification of acetic acid, but its influence was found to be far less than that of oxalic acid or of picric acid.

The author has prepared the corresponding alkyl bromides from ethyl, propyl, *iso*butyl, and allyl alcohols by distilling them with the hydrate of hydrogen bromide, $HBr,5H_2O$. In these reactions the yield was greatly increased, except in the case of allyl alcohol, by replacing the hydrogen bromide hydrate by a mixture of this hydrate with sulphuric acid, obtained by passing sulphur dioxide into a mixture of bromine and water in suitable proportions until it was just decolorised. The yields obtained by this method varied from 75—90% of the theoretical amount. *iso*Butyl alcohol gave a mixture of primary and tertiary *iso*butyl bromides. W. G.

Preparation of Ethyl Acetate from Acetaldehyde. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 277188. Add. to D.R.-P. 277187; from *J. Soc. Chem. Ind.*, 1915, **34**, 152).—In the

preparation of ethyl acetate from acetaldehyde by the process described in the chief patent (this vol., i, 3), the aluminium alkyloxide catalyst is used in solution, preferably in ethyl acetate. The aldehyde may be added to the solvent used for dissolving the catalyst.

C. S.

The System: Lead Oxide—Acetic Acid—Water. SHIGEHISA SAKABI (*Mem. Coll. Sci. Kyoto*, 1914, **1**, 57—61).—A systematic examination of the equilibrium relations at 25° has shown that the only solid compounds which can exist in contact with solutions at this temperature are the normal salt $Pb(C_2H_3O_2)_2,3H_2O$ and the basic salts $Pb(C_2H_3O_2)_2,Pb(OH)_2$ and $Pb(C_2H_3O_2)_2,2Pb(OH)_2$. The solution in equilibrium with the first two compounds has the composition—water 86·90%, acetic acid 7·92%, lead oxide 5·18%, whilst that of the solution in equilibrium with the two basic salts is water 85·59%, acetic acid 7·26%, lead oxide 7·15%. The complete data are utilised in the construction of a triangular graph, which shows clearly the general nature of the solubility relations. H. M. D.

Oxidation of Oils and Fatty Acids. J. HYLAND and L. L. LLOYD (*J. Soc. Chem. Ind.*, 1915, **34**, 62—65).—The object of the investigation is the valuation of the partially hydrogenated oils which are being placed on the market as substitutes for olive oil, for use in the worsted trade, etc.

The production of sulphuric acid by the action of sulphur dioxide and oxygen on oils for a definite time at a constant temperature is constant for some oils, but for many others, particularly those which char in contact with sulphuric acid, concordant results cannot be obtained. The yield of sulphuric acid is greatly increased in the presence of a drier, the increase varying with the amount and the nature of the drier. The order of activity, calculated from the production of sulphuric acid, of the metals which have been tested when dissolved as resinates in the oils, is as follows—copper, cobalt, manganese, nickel, chromium, and iron. It has also been observed that the addition of small amounts of oxidisable oils to "non-drying oils" greatly increases the rate at which these oils absorb oxygen, and affects the amount of sulphuric acid formed by the action of sulphur dioxide and oxygen.

The authors have made a series of experiments in which oleic acid, ethyl oleate, and olive oil, each alone, and also in the presence of 5% of manganese resinate, have been oxidised in a current of air (usually, moist air at 50°) until the maximum increase in weight has been attained; the iodine values have been determined before and after the oxidation. The results show that the ratio between the increase in weight and the diminution in the iodine value corresponds with $O_2=I_2$, and also that the oxidation products of ethyl oleate and of olive oil are more stable than those of oleic acid.

In connexion with the preceding, a comparison has been instituted between the iodine value of an oil and its liability to firing. It appears that the iodine value is of little use as a guide to liability to firing. Although firing is due primarily to oxidation, it is affected

by other factors such as acidity, the constitution of the fatty acids, and the decomposition of the oxidation products. Ethyl oleate is far safer than the free acid, probably on account of the greater stability of its oxidation products. The most dangerous oils are those the oxidation products of which are most easily decomposed or polymerised.

C. S.

Polymerised Drying Oils. R. S. MORRELL (*J. Soc. Chem. Ind.*, 1915, **34**, 105—109).—Various drying oils have been thickened by heating, usually in an atmosphere of carbon dioxide to avoid oxidation; for example, linseed oil has been heated at 260—280° for twenty-eight to sixty hours, and tung oil (Chinese wood oil) at 240° for twenty minutes. The density, refractive index, molecular weight (in benzene), acidity, saponification value, iodine number, and percentage of glyceryl in the thickened and unthickened oils have been determined. Also the methyl esters prepared from thickened linseed oil by Ball's method have been examined. The following conclusions have been drawn from the data thus acquired. (1) Linseed and poppy-seed oils contain mixed glycerides of variable amounts of unsaturated acids, in addition to small quantities of saturated glycerides, the acids being interchangeable, and their amounts are dependent on the sources, and probably on the ripeness, of the seeds. (2) Thickening by polymerisation without change in chemical composition occurs when there are at least two pairs of doubly linked carbon atoms in the molecules of the acids of the glycerides. (3) Before polymerisation occurs, there is a shifting of the linkings in the molecule, and, in the case of tung oil, there is some slight evidence of ring formation. (4) Thickening is due to polymerisation of the mixed glycerides, and the first stage is the formation of a product insoluble in acetone, which may be a double molecule of linked glycerides in the case of linseed oil, or a quadruple molecule in poppy-seed oil. (5) The change depends on the temperature, and equilibrium is established when 50% of the modification has been formed. (6) At higher temperatures the final stage is the formation of a polymeride insoluble in light petroleum, which seems to be determined in linseed oil by the linolenic acid glyceride.

A comparison of the properties of olive oil and heated olive oil shows that the evidence of isomeric change in a non-drying oil is very slight.

C. S.

Ammonium Citrate. ROBERT A. HALL (*J. Amer. Chem. Soc.*, 1915, **37**, 208—216).—A quantitative yield of normal ammonium citrate, $(NH_4)_3C_6H_5O_7$, can be readily obtained by passing dry ammonia into a boiling solution of anhydrous citric acid in absolute alcohol. The salt thus prepared is crystalline and stable; it is very soluble in water but cannot be recrystallised from aqueous solutions. When a saturated solution, cooled by means of a mixture of ice and salt, is poured into absolute alcohol, similarly cooled, a mass of long, slender crystals is obtained which probably consists of ammonium citrate with one or more molecules of water of crystallisation. Aqueous solutions of normal ammonium citrate give an alkaline reaction with rosolic

acid. A solution D^{20} 1·09, can be substituted for the so-called "neutral" ammonium citrate solutions employed in estimating the insoluble phosphates in commercial fertilisers. E. G.

Esters and Unimolecular β- and γ-Lactones of *d*-Mannonic and *d*-Gluconic Acids; *o*-Bis-*d*-galactonic Acid, *d*-Galactono-γ-lactone and its Monohydrate. Oscar F. Hedenburg (*J. Amer. Chem. Soc.*, 1915, **37**, 345—372).—A detailed account is given of certain experiments, the chief results of which have already been recorded by Nef (A., 1914, i, 491, 492, 497).

Ethyl *d*-mannonate has m. p. 160—161°. *d*-Glucono-β-lactone has m. p. 153°, and $[\alpha]_D^{20}$ + 63·4° after it has been in solution for five minutes. Ethyl *d*-gluconate has m. p. 62—63°. *d*-Glucono-γ-lactone has m. p. 134—136° and $[\alpha]_D^{20}$ + 67·52° after it has been in solution for nine minutes. *d*-Galactono-γ-lactone has m. p. 108—111° and $[\alpha]_D^{20}$ − 76·97°; the monohydrate has m. p. 66° and $[\alpha]_D^{20}$ − 70·1°. E. G.

Biochemical Synthesis by Means of Emulsin of the β-Monoglucoside of Ordinary Propylene Glycol. Em. Bourquelot, M. Bridel, and A. Aubry (*Compt. rend.*, 1915, **160**, 214—216).—Propane-αβ-diol has been converted into its monoglucoside by dissolving in it one quarter of its weight of dextrose, adding a little water and some emulsin, and allowing the mixture to remain for six months at 33°. At the end of this time it was heated on a water-bath for twenty minutes and then the water and unchanged glycol distilled off under reduced pressure. The unchanged dextrose was removed from the residue by solution in water and fermenting with top yeast. The residue finally obtained after this treatment still contained some unchanged glycol which was removed by five successive extractions with ethyl acetate. Attempts to obtain the colourless, transparent residue in a crystalline form by precipitation with ether from alcoholic solution were unsuccessful. So purified, however, it had $[\alpha]_D$ − 30·32°, and analysis showed it to be a *monoglucoside*. It was readily hydrolysed either by dilute sulphuric acid, or by emulsin in aqueous solution, the product being in each case *i*-propane-αβ-diol. W. G.

Diverse Colloidal States of Starch. Max Samec (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 173—188. Compare A., 1912, ii, 144; 1913, i, 17, 1155; 1914, i, 930).—A summary of work previously published. H. W. B.

Oxycellulose. Wilder D. Bancroft (*J. Physical Chem.*, 1915, **19**, 159—168).—Experiments have been made to ascertain to what extent the properties of oxycellulose or the oxycelluloses differ when prepared by the action of nitric acid, permanganate, chloric acid, and bleaching powder on cellulose. The results obtained afford no evidence for the existence of three different oxycelluloses. The substance described as α-oxycellulose is apparently unchanged cellulose, more or less contaminated with certain products of decomposition. Except in regard to

the degree of agglomeration, β- and γ-oxycellulose appear to be identical.

None of the above oxidising agents gives a completely oxidised product, and it is doubtful whether a pure oxycellulose has as yet been obtained. The reducing action on Fehling's solution is not a characteristic of oxycellulose, but is probably due to other products of the oxidation reaction. Experiments with a number of metallic mordants indicate that these are not absorbed to any large extent.

H. M. D.

Introduction of the Guanidine Nucleus into the Molecule of Polypeptides. I. ANTONINO CLEMENTI (*Gazzetta*, 1915, **45**, i, 56—59).—*Glycocyamylglycine*, $NH:C(NH_2)\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, prepared by the action of cyanamide on glycylglycine in presence of ammonia, forms microscopic, white needles, which turn brown at 218—220° and decompose at about 235°. It yields negative results with the biuret reagent and with sodium nitroprusside. T. H. P.

Complex Ions of Nickel and Cobalt with Cyanogen. G. ROSSI (*Gazzetta*, 1915, **45**, i, 6—10).—The maximal electrical conductivities attained on gradual addition of potassium cyanide solution to solutions of nickel and cobalt chlorides correspond with the formation of the complex ions, $Ni(CN)_4$ and $Co(CN)_6$, the salts formed having the formulæ, $K_2Ni(CN)_4$ and $K_4Co(CN)_6$ respectively. T. H. P.

Melting Point of 2 : 4 : 6-Trinitrotoluene. WILLIAM RINTOUL (*J. Soc. Chem. Ind.*, 1915, **34**, 60—61).—Values between 78·85° and 82° have been recorded by various observers as the m. p. of 2 : 4 : 6-trinitrotoluene. The author has obtained the following values, using carefully purified materials and recrystallising each nitro-compound until the m. p. of the last crop of crystals is the same as that of the solid obtained by evaporating the mother liquor : *p*-nitrotoluene, m. p. 51·6—51·9°; 2 : 4-dinitrotoluene, m. p. 69·9—70·2°; 2 : 4 : 6-trinitrotoluene, m. p. 80·80—80·85°.

The most efficient method of purifying commercial trinitrotoluene is crystallisation from alcohol or benzene. C. S.

Action of Chloral, Bromal, and Benzaldehyde on the Polycyclic Hydrocarbons in the Presence of Aluminium Chloride. II. G. B. FRANKFORTER and W. KRITCHEVSKY (*J. Amer. Chem. Soc.*, 1915, **37**, 385—392).—In an earlier paper (A., 1914, i, 1059) it has been shown that, in presence of aluminium chloride, chloral reacts violently with benzene and its derivatives at the ordinary temperature whilst at low temperatures a condensation takes place. The study of this reaction has now been extended to the polycyclic hydrocarbons.

Chloral reacts very energetically with naphthalene, but if the temperature is not allowed to rise above 0° a nearly quantitative condensation is effected with formation of a mixture of dichloro-*αα*-dinaphthylethylene, $C(C_{10}H_7)_2:CCl_2$, m. p. 147—148°, and dichloro-*ββ*-dinaphthylethylene, m. p. 219°.

By the action of bromal on naphthalene at 0° in presence of alu-

minium chloride, dibromo-*ββ*-dinaphthylethylene, $C(C_{10}H_7)_2{:}CBr_2$, m. p. 223—225°, is produced which forms colourless crystals.

By the action of chloral on anthracene in presence of aluminium chloride and light petroleum, *ββ-dichlorodianthrylethylene*, $C(C_{14}H_9)_2{:}CCl_2$, is obtained as a brownish-yellow powder. When heated it darkens and begins to decompose at 340°. If benzene is employed instead of light petroleum, a different reaction occurs, and *ββ-dichloro*-9 : 10-*anthrenylethylene*, $C_{14}H_8{:}C{:}CCl_2$, is produced as a yellow, amorphous powder. When carbon disulphide is used as the solvent, a third reaction takes place with production of *βββ-trichloro*-9 : 10-*anthrenylethane*, $C_{14}H_8{:}CH{\cdot}CCl_3$, which forms a yellowish-brown powder.

When anthracene is treated with bromal in presence of aluminium chloride and carbon disulphide, *βββ-tribromo*-9 : 10-*anthrenylethane*, $C_{14}H_8{:}CH{\cdot}CBr_3$, is obtained as a chocolate-brown powder which does not melt at 360°.

By the action of chloral on phenanthrene in presence of aluminium chloride and carbon disulphide, *βββ-trichloro*-9 : 10-*phenanthrenylethane*, $C_{14}H_8{:}CH{\cdot}CCl_3$, is produced as a yellow powder without a definite m. p. *βββ-Tribromo*-9 : 10-*phenanthrenylethane*, $C_{14}H_8{:}CH{\cdot}CBr_3$, formed by the action of bromal under similar conditions, is a yellow powder which can be heated at 300° without change.

By the action of benzaldehyde on phenanthrene in presence of aluminium chloride and carbon disulphide, there are produced *phenyldiphenanthrylmethane*, $CHPh(C_{14}H_9)_2$, m. p. 165° (decomp.), which forms a dark yellow powder, and *dibenzylidenemesotriphenanthrene*, $C_{14}H_8(CHPh{\cdot}C_{14}H_9)_2$, m. p. 195—197° (decomp.), obtained as a brown powder. E. G.

Molecular Weights of the Hydroxybenzoic Acids. W. Œchsner de Coninck (*Compt. rend.*, 1915, **160**, 67—68. Compare A., 1914, i, 95).—The author has determined the molecular weights of salicylic acid by analysis of its pure calcium and ammonium salts, and of *m*- and *p*-hydroxybenzoic acids by analysis of their pure ammonium salts. The mean value for all the determinations is 137·986. W. G.

Tautomerism of Phenylpyruvic Acid. J. Bougault and (Mlle.) R. Hemmerlé (*Compt. rend.*, 1915, **160**, 100—102. Compare *Bull. Soc. Chim.*, 1914, [iv], **15**, 529).—The authors bring forward further experimental results in support of the view that phenylpyruvic acid exists in two tautomeric forms, the free acid being in the enolic form and the normal salts in the ketonic form.

A 10% solution of sodium phenylpyruvate does not give a precipitate immediately on the addition of hydrochloric acid, although the free acid is insoluble in water. A precipitation slowly occurs as the unstable ketonic form passes into the stable enolic form.

On dissolving phenylpyruvic acid in an aqueous solution of potassium hydrogen carbonate, and then acidifying with acetic acid, a partial precipitation of the enolic form of the free acid occurs, but on leaving the mixture, this precipitate slowly dissolves, the enolic form of the acid passing to the soluble ketonic form.

A freshly prepared solution of phenylpyruvic acid (0·04 gram) in 1 c.c. of 4% aqueous potassium hydrogen carbonate required 2·2 c.c. of a solution of potassium permanganate to colour it permanently, whereas 1 c.c. of the same solution after remaining twenty-four hours only required a few drops of the permanganate.

A solution of sodium phenylpyruvate (0·34 gram) in 5 c.c. of water to which were added in turn 5 c.c. of ether, 0·5 c.c. of concentrated hydrochloric acid, and 0·2 gram of semicarbazide hydrochloride, gave an abundant precipitate of a semicarbazone, insoluble in water and very soluble in ether, whereas free phenylpyruvic acid under the same conditions gave no trace of semicarbazone.

The authors show that small quantities of alkali can, like the acids and more rapidly than them, convert the ketonic form into the enolic form.

Finally, as a proof of the existence of the enolic form they have obtained an *acetate* having the constitution $CHPh{:}C(OAc)\cdot CO_2H$, b. p. 168°, by boiling either the free acid or its sodium salt with acetic anhydride. W. G.

3-Nitro-4-hydroxycinnamic Acid and its Methyl Ether. Treat B. Johnson and Edward F. Kohmann (*J. Amer. Chem. Soc.*, 1915, **37**, 162—167).—During the course of an investigation of nitrated protein, specimens of 3-nitro-4-hydroxycinnamic acid and its methyl ether were required for purposes of identification, and the compounds were therefore prepared by Einhorn and Grabfield's method (A., 1888, 477).

Nitroanisaldehyde (3-nitro-4-methoxybenzaldehyde), m. p. 83°, can be readily obtained by Einhorn and Grabfield's method (*loc. cit.*) if the temperature is kept below 0°; at higher temperatures, however, a product results which has m. p. about 73°, and seems to be a mixture of mono- and di-nitroanisaldehyde. 3-Nitro-4-hydroxycinnamic acid has m. p. 223°, and its methyl ether, m. p. 247—248°; Einhorn and Grabfield have given the m. p.'s of these compounds as 198° and 140° respectively.

Ethyl 3-nitro-4-hydroxycinnamate has m. p. 110—111°; the *methyl* ester, m. p. 142—144°, crystallises in rosettes of slender, yellow needles.

When 3-nitro-4-hydroxycinnamic acid methyl ether is treated with a solution of bromine in ether, no reaction takes place (compare Einhorn and Grabfield, *loc. cit.*), but on treatment with bromine dissolved in glacial acetic acid, it readily yields 3-nitro-4-methoxyphenyl-$\alpha\beta$-dibromopropionic acid. E. G.

Valency of Nitrogen in Ammonium Salts. William A. Noyes and Ralph S. Potter (*J. Amer. Chem. Soc.*, 1915, **37**, 189—203).—An account is given of the preparation of certain amino-derivatives of camphoric acid. A study of the specific rotation of these substances has indicated that amino-acids, which can form cyclic salts containing quinquevalent nitrogen and a ring of six atoms, form salts of the general formula $R<^{CO--}_{NH_3}>O$ in aqueous solutions.

Amino-acids, which would give a ring of seven atoms in forming a cyclic salt, seem to exist in solution as compounds of the form $NH_2 \cdot R \cdot CO_2H$. These relations afford evidence that nitrogen is quinquevalent in ammonium salts, and that the hydrogen of the acid combines with the nitrogen instead of remaining united to the acid radicle, as has been supposed by Werner.

Amino-camphonanic acid has $[\alpha]_D^{25} - 29{\cdot}2°$, and its anhydride $[\alpha]_D^{29} - 60{\cdot}5°$. On hydrolysing the anhydride with 20% hydrochloric acid, aminocamphonanic acid hydrochloride is produced, which has $[\alpha]_D^{24} + 24{\cdot}9°$. The *acetyl* derivative of the anhydride, $C_8H_{14}<\begin{matrix}CO\\|\\NAc\end{matrix}$, has b. p. 260—262°, and $[\alpha]_D + 72{\cdot}7°$; the nitroso-derivative has $[\alpha]_D^{24} + 153°$.

α-Amino-campholic acid decomposes at 300—320° without melting, and has $[\alpha]_D^{26} + 67{\cdot}6°$; its hydrochloride has m. p. 248—250° and $[\alpha]_D^{24} + 44{\cdot}7°$. α-Camphidone has m. p. 230—231° and $[\alpha]_D^{25} - 33{\cdot}9°$; its *nitroso*-derivative, $C_8H_{14}<\begin{matrix}CO\\CH_2\end{matrix}>N \cdot NO$, has m. p. 125—126° and $[\alpha]_D^{23} - 59{\cdot}0°$.

Aminodihydrocampholytic acid has $[\alpha]_D^{25} + 54{\cdot}7°$, and its hydrochloride $[\alpha]_D^{26} + 41{\cdot}3°$. The nitroso-derivative of amino-campholytic anhydride has $[\alpha]_D^{25} - 83{\cdot}3°$.

Cyanodihydrocampholytic acid has $[\alpha]_D^{22} + 25{\cdot}3°$. β-Aminocampholic acid has $[\alpha]_D^{25} + 16{\cdot}4°$, and its hydrochloride m. p. 218—220° and $[\alpha]_D^{26} + 41{\cdot}3°$. β-Camphidone has m. p. 234—235° and $[\alpha]_D^{24} + 63{\cdot}2°$; its *nitroso*-derivative, $C_8H_{14}<\begin{matrix}CH_2\\CO\end{matrix}>N \cdot NO$, has m. p. 164—165° and $[\alpha]_D^{23} + 103°$. E. G.

Bismuth Salts of Halogenated Derivatives of Gallic Acid. P. Lami (*Boll. Chim. Farm.*, 1914, **54**, 2—5).—*Basic bismuth dichlorogallate*, $C_6Cl_2(OH)_3 \cdot CO_2 \cdot Bi(OH)_2$, prepared from dichlorogallic acid, m. p. 155°, is almost lemon-yellow and of no therapeutic value. *Basic bismuth dibromogallate*, $C_7H_5O_7Br_2Bi$, prepared from dibromogallic acid, m. p. about 150°, is olive-green, and *basic bismuth di-iodogallate*, $C_7H_5O_7I_2Bi$, dark yellow. These two salts are soluble in concentrated sulphuric acid, with formation of a red and then a black coloration and evolution of vapours of the halogen. Both are useful in dermatology and act as local astringents. T. H. P.

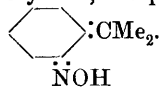
Additive Compounds of Aldehydes and Ketones with Organic Acids. James Kendall and Willis A. Gibbons (*J. Amer. Chem. Soc.*, 1915, **37**, 149—162).—In earlier papers (A., 1914, i, 858, 1069) it has been shown that dimethylpyrone yields additive compounds with organic acids which vary in stability according to the strength of the acid used.

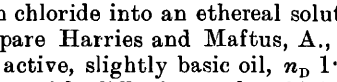
A study has now been made of the f. p. curves of trichloracetic acid with various aldehydes and ketones. Of the aldehydes, salicylaldehyde, *m*-hydroxybenzaldehyde, *o*-, *m*-, and *p*-nitrobenzaldehydes, and nitropiperonaldehyde did not yield additive compounds. Benzaldehyde furnished the *compound*, $C_6H_5 \cdot CHO, CCl_3 \cdot CO_2H$, m. p. 8·4°; *p*-hydroxybenzaldehyde, the *compound*, $OH \cdot C_6H_4 \cdot CHO, CCl_3 \cdot CO_2H$, m. p. 67·8°;

anisaldehyde, the *compound*, $OMe\cdot C_6H_4\cdot CHO,CCl_3\cdot CO_2H$, m. p. 30·9°; vanillin, the *compounds*, $OMe\cdot C_6H_3(OH)\cdot CHO,2CCl_3\cdot CO_2H$, m. p. 14·3°, $OMe\cdot C_6H_3(OH)\cdot CHO,CCl_3\cdot CO_2H$, m. p. 23°, and $2OMe\cdot C_6H_3(OH)\cdot CHO,CCl_3\cdot CO_2H$, m. p. 45°; and piperonaldehyde, the *compounds*, $C_8H_6O_3,2CCl_3\cdot CO_2H$, m. p. 37·4°, and $C_8H_6O_3,CCl_3\cdot CO_2H$, m. p. 35°. Of the ketones, additive compounds could not be isolated in the case of benzophenone, phenyl anisyl ketone, benzil, and benzoquinone, but acetophenone yielded the *compound*, $C_6H_5\cdot CO\cdot Me,CCl_3\cdot CO_2H$, m. p. 26°, and distyryl ketone, the *compounds*, $C_{17}H_{14}O,2CCl_3\cdot CO_2H$, m. p. 86·5°, and $C_{17}H_{14}O,CCl_3\cdot CO_2H$, m. p. 117°. A few of these aldehydes and ketones were also investigated with chloroacetic and benzoic acids, but in no case was there any indication of the formation of additive compounds.

The results of this work confirm the view expressed in the earlier papers that the reaction is ionic and that the compounds formed are oxonium salts. E. G.

Anhydrohydroxylamines of Unsaturated Ketones. L. Francesconi and G. Sanna (*Gazzetta*, 1915, **45**, i, 35—41).—The authors find that the tendency to form anhydro-bases similar to that obtained by Semmler (A., 1904, i, 437, 602) from pulegonehydroxylamine is exhibited generally by unsaturated, cyclic, $\alpha\beta$-ketones having the double linking outside the nucleus and by unsaturated $\alpha\beta$-ketones of the aliphatic series. These anhydro-bases may be obtained by Harries and Jablonski's method (A., 1898, i, 400), but the compound described by these authors as an *iso*oxazole derivative is more probably an imino-base.

The action of dry hydrogen chloride on pulegonehydroxylamine in ethereal solution gives a small yield of the base prepared by Semmler (*loc. cit.*), but prolongation of the action results in the formation of an *oxime*, which separates in tufts of prismatic crystals, m. p. 141°, and appears to be the normal oxime of pulegone,  .

Anhydrocamphoronehydroxylamine,  , prepared by passing dry hydrogen chloride into an ethereal solution of camphoronehydroxylamine (compare Harries and Maftus, A., 1899, i, 629), is obtained as an optically active, slightly basic oil, n_D 1·468; it forms a *picrate* which crystallises with difficulty and exhibits many of the reactions of alkaloids. T. H. P.

Derivatives of 1 : 2 : 3 : 5-Tetrahydroxybenzene. G. Bargellini (*Gazzetta*, 1915, **45**, i, 85—93).—The action of propionyl chloride, in presence of sublimed aluminium chloride, on 1 : 2 : 3 : 5-tetramethoxybenzene (compare Bargellini and Bini, A., 1911, i, 211) dissolved in carbon disulphide yields: (1) 2 : 3 : 4 : 6-*Tetrahydroxypropiophenone trimethyl ether*, $OH\cdot C_6H(OMe)_3\cdot COEt$, which forms straw-yellow, prismatic crystals, m. p. 124—126°, and with ferric

chloride in alcoholic solution gives a yellowish-brown coloration and with concentrated sulphuric acid a yellow solution becoming deep violet when heated. Its *acetyl* derivative, $C_{14}H_{18}O_6$, forms white needles, m. p. 73—74°. (2) 2 : 3 : 4 : 6-*Tetramethoxypropiophenone*, $C_6H(OMe)_4 \cdot COEt$, which may also be obtained by the action of methyl sulphate on the preceding compound; it forms white crystals, m. p. 55—56°, and dissolves in concentrated sulphuric acid, giving a yellow coloration which turns deep violet on heating.

Under similar conditions, the action of benzoyl chloride on 1 : 2 : 3 : 5-tetramethoxybenzene yields: (1) 2 : 3 : 4 : 6-*Tetrahydroxybenzophenone trimethyl ether*, $OH \cdot C_6H(OMe)_3 \cdot COPh$, which forms white crystals, m. p. 87—89°, and gives an intense reddish-brown coloration with ferric chloride in alcoholic solution; with concentrated sulphuric acid it gives first a bright red coloration and then a yellow solution, which changes to green and afterwards to deep violet when heated. Its *acetyl* derivative, $C_{18}H_{18}O_6$, forms white needles, m. p. 130—132°. (2) 2 : 3 : 4 : 6-*Tetramethoxybenzophenone*, $C_6H(OMe)_4 \cdot COPh$, which forms white crystals, m. p. 125—126°; with concentrated sulphuric acid it behaves similarly to the preceding compound. T. H. P.

Blue Hydrocarbon Occurring in Some Essential Oils. ALFRED E. SHERNDAL (*J. Amer. Chem. Soc.*, 1915, **37**, 167—171).—Several essential oils yield blue fractions, boiling between 275° and 300°, and it has usually been supposed that their colour is due to the presence of a blue compound, consisting of an oxygenated substance related to the sesquiterpene alcohols.

The compound has now been isolated by shaking a very blue fraction with 63% sulphuric acid, in which it is soluble. The acid liquid was diluted and extracted with light petroleum. The blue solution in light petroleum was then shaken with 85% phosphoric acid, and the dark red acid solution thus obtained was diluted and extracted with ether. On evaporating the ethereal solution, a residue was obtained, consisting of an intensely blue, slightly viscid liquid, with a faint, thymol-like odour. This substance is a *hydrocarbon*, $C_{15}H_{18}$, which has D_{25} 0·9738, and boils at 185—195°/25 mm., or at 295—300° under ordinary pressure, leaving a brown, tarry residue; when exposed to light and air, it is gradually converted into a brown resin. The author proposes to term the substance *azulene*, a name originally assigned by Piesse to a blue fraction obtained from oil of wormwood. Solutions of the compound in mineral acids are strongly fluorescent. By the action of acetic anhydride and sulphuric acid, the hydrocarbon is converted into a *sulphonic acid*, which yields a crystalline *sodium* salt. The aqueous solution of the sodium salt is violet, but becomes pale green when acidified; it yields precipitates with solutions of calcium or barium salts, and is decolorised by bromine water. E. G.

Turpentine and Turpentine Oil of Aleppo Pine. D. E. TSAKALOTOS (*J. Pharm. Chim.*, 1915, [vii], **11**, 70—72).—A sample of turpentine (resinous exudation) collected from Aleppo pines (*Pinus halepensis*) growing in Attica, Greece, yielded the following percentage

results on analysis: turpentine oil 21·4, dry residue 70·8, solid impurities 4·5, water and loss 3·3 (compare A., 1909, i, 818). The turpentine oil consisted almost entirely of *d*-pinene. W. P. S.

Oils of the Coniferæ. IV. The Leaf and Twig Oils of Digger Pine, Lodgepole Pine, and Red Fir. A. W. SCHORGER (*J. Ind. Eng. Chem.*, 1915, **7**, 24—26. Compare A., 1914, i, 1203).—The physical and chemical constants of the leaf and twig oils of the digger pine (*Pinus sabiniana*), the lodgepole pine (*Pinus contorta*), and the red fir (*Abies magnifica*) were found to be as follows: Digger pine, yield, 0·078 to 0·102%; D^{15} 0·8517 to 0·8566; n_D^{15} 1·4670 to 1·4708; α_D^{20} −20·93° to −38·36°; acid number 1·47 to 2·05; ester number, 6·77 to 11·98. Lodgepole pine, yield, 0·234%; D^{15} 0·8690; n_D^{15} 1·4381; α_D^{20} −17·84°; acid number, 0·90; ester number, 6·02. Red fir, yield, 0·154%; D^{15} 0·8665; n_D^{15} 1·4861; α_D^{20} −16·70°; acid number, 0·75; ester number, 9·93. The percentage composition of the oils was:

	Digger pine.	Lodgepole pine.	Red fir.
Furfuraldehyde	—	trace	trace
n-Heptane	3	—	—
l-α-Pinene	58—59	3	?
l-Camphene	—	5—6	—
l-β-Pinene	—	49—50	16—18
l-Phellandrene	—	19	52
Dipentene	—		0
l-Limonene	18	—	—
Bornyl ester (as acetate)	3·5	2	3·5
Free alcohol (*l*-borneol)	6	7·5	7·5
Methylchavicol	?	?	—
"Green oil"	2—3	—	13
Cadinene	—	7	—
Loss, etc.	9·5	6	6

W. P. S.

Tormentole, the Extractive Principle of Potentilla Tormentilla. A. GORIS and CH. VISCHNIAC (*Compt. rend.*, 1915, **160**, 77—80).—*Tormentole* can be extracted from the fresh or dried roots of *Potentilla Tormentilla*, by powdering the roots, moistening them with basic lead acetate solution, and extracting the mass three times with boiling acetone and filtering. The extract is cooled and the lead compounds and a yellow oil allowed to separate. The clear acetone solution is decanted, and excess of water added. The precipitate is collected, dissolved in cold alcohol, and the solution purified with basic lead acetate, the excess of lead being removed by sulphuric acid (10%). The liquid is finally distilled under reduced pressure until crystallisation occurs, the crystalline product being recrystallised from dilute alcohol. Tormentole so obtained crystallises in slender needles, m. p. 227—228°, to which provisionally the formula $C_{33}H_{50}O_{10},5H_2O$ is assigned. It is a neutral, saturated substance, containing an hydroxyl group, and being also an ester. It loses its $5H_2O$ at 100° or on drying over sulphuric acid in a vacuum, the anhydrous product obtained in the first case being yellow in colour and

non-crystallisable. The rotatory power of the hydrated substance varies with the solvent, being in alcohol, $[\alpha]_D$ +10·78° and in acetic acid, $[\alpha]_D$ +20·77°, these being calculated for the anhydrous product. The anhydrous product obtained at 100° has $[\alpha]_D$ +32·13° in alcohol and +33·03° in acetic acid. On saponification with alcoholic potassium hydroxide, tormentole yielded an *alcohol*, m. p. 310° and an *acid*, m. p. 280°, neither of which has, as yet, been characterised. Tormentole is esterified on heating with acid anhydrides, but in every case a mixture of products, which could not be separated, was obtained. W. G.

Chlorophyll. RICHARD WILLSTÄTTER (*J. Amer. Chem. Soc.*, 1915, **37**, 323—345).—A review of the work hitherto carried out on chlorophyll. The methods employed in the investigations are described, an account is given of the isolation of chlorophyll and its separation into its components, and the constitution of the substance is discussed. E. G.

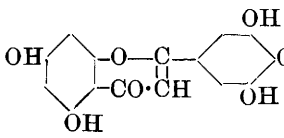
Coumarins. G. BARGELLINI and LYDIA MONTI (*Gazzetta*, 1915, **45**, i, 90—98. Compare A., 1911, i, 855).—Various coumarin derivatives have been subjected to the action of potassium persulphate in alkaline solution, with a view to determining their constitutions.

With coumarin itself, this treatment yields only 5-hydroxycoumarin. With 4-methoxycoumarin (umbelliferone methyl ether), 5-hydroxy-4-methoxycoumarin, identical with the monomethyl ether, m. p. 184°, formed on partial methylation of æsculetin, is obtained. Scopoletin, m. p. 204°, which is also an æsculetin monomethyl ether, must consequently be 4-hydroxy-5-methoxycoumarin, as, indeed, was demonstrated by Moore (T., 1911, **99**, 1043). T. H. P.

Constitution and Synthesis of Scutellarein. G. BARGELLINI (*Gazzetta*, 1915, **45**, i, 69—79).—*2 : 3 : 4 : 6-Tetramethoxybenzoyl-4-methoxyacetophenone*, $C_6H(OMe)_4 \cdot CO \cdot CH_2 \cdot CO \cdot C_6H_4 \cdot OMe$, prepared by the condensation of 2 : 3 : 4 : 6-tetramethoxyacetophenone (compare Bargellini and Bini, A., 1911, i, 211) with methyl anisate in presence of sodium, forms yellowish crystals, m. p. 104—106°, and, in alcoholic solution, gives a garnet-red coloration with ferric chloride. When heated with hydriodic acid this compound undergoes demethylation and then loses the elements of water with formation, as sole product, of a compound which must be either 5 : 7 : 8 : 4′- or 5 : 6 : 7 : 4′-tetrahydroxyflavone. As this compound is identical with natural scutellarein, these results confirm the constitution of the latter deduced by Goldschmiedt and Zerner (A., 1910, i, 576). An attempt is now being made to decide between the two alternative structures. T. H. P.

Pentahydroxyflavone. G. BARGELLINI and LYDIA MONTI (*Gazzetta*, 1915, **45**, i, 64—69).—With the object of devising a general method for the conversion of flavones into flavonones and thence into flavanols, the authors have attempted to apply the results of their investigations on the transformation of phenyl styryl ketones into phenyl phenylethyl ketones (compare this vol., i, 19).

3 : 4 : 5-*Trimethoxybenzoyl*-2 : 4 : 6-*trimethoxyacetophenone*, $C_6H_2(OMe)_3 \cdot CO \cdot CH_2 \cdot CO \cdot C_6H_2(OMe)_3$, prepared by the condensation of 2 : 4 : 6-trimethoxyacetophenone with the trimethyl ether of methyl gallate in presence of sodium, forms white crystals, m. p. 136—138°, and gives a red coloration with ferric chloride in alcoholic solution, whilst with concentrated sulphuric acid it gives, first a red coloration, and then a yellow solution. When the methyl groups of this compound are removed by treatment with boiling hydriodic acid, the enolic modification of the resulting hexahydroxybenzoylacetophenone loses the elements of water, yielding, 5 : 7 : 3′ : 4′ : 5′-*pentahydroxyflavone* (annexed formula), which forms a yellow, crystalline powder, blackening and gradually decomposing at above 270°; with ferric chloride it forms a greenish brown-yellow coloration and it dissolves in sodium hydroxide solution giving an orange-red, and in concentrated sulphuric acid giving a yellow, coloration. The corresponding *penta-acetyl*-derivative, $C_{25}H_{20}O_{12}$, forms white needles, m. p. 216—218°. Attempts to prepare a methyl ether of the pentahydroxyflavone resulted in the formation of a small proportion of a product, m. p. 112—118°, which is probably the 5 : 3′ : 4′ : 5′-tetramethyl derivative.



Hydrogenation of the double linking of 5 : 7 : 3′ : 4′ : 5′-pentahydroxyflavone or its penta-acetyl derivative could not be effected in the conditions successfully employed with the phenyl styryl ketones, namely, under slight pressure and in presence of palladium black. Attempts to hydrogenate 6 : 7-dimethoxyflavone, its diacetyl derivative, and its dimethyl ether (compare Reigrodski and Tambor, A., 1910, i, 578) were also unsuccessful. T. H. P.

Sempervirine, a Third Alkaloid from Gelsemium. A. E. Stevenson and L. E. Sayre (*Pharm. J.*, 1915, **94**, 159; from *J. Amer. Pharm. Assoc.*, 1915, 60).—A substance, described as a third alkaloid, has been isolated from gelsemium by extracting a large quantity of the latter with alcohol, evaporating the alcoholic solution to a syrup, and shaking this with chloroform; the chloroform solution was then evaporated to a small volume, which was shaken with dilute hydrochloric acid and the acid solution then shaken with benzene to remove gelsemic acid. The acid solution was next shaken with chloroform, the chloroform solution evaporated, the residue extracted with water, the aqueous solution evaporated to dryness, the residue dissolved in alcohol, mixed with sand, again evaporated to dryness, and the powder extracted first with acetone and then with alcohol. On evaporating this alcoholic solution, the hydrochloride of the alkaloid separated in the form of crystals. The salts of the alkaloid are very insoluble in dilute acids; the addition of nitric acid to an aqueous solution of the hydrochloride precipitates the salt so completely that the supernatant liquid yields only a faint opalescence with Mayer's reagent. The nitrate is sparingly soluble in alcohol and crystallises from it in the form of yellow needles, m. p. about 280° (decomp.); the alkaloid itself, prepared from the recrystallised nitrate

occurs as pale yellow crystals. The hydrochloride is readily soluble in alcohol. Gelsemium contains only very small quantities of this alkaloid, for which the name *sempervirene* is suggested. W. P. S.

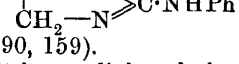
Struxine, a New Alkaloid in Nux Vomica. H. H. SCHAEFER (*Pharm. J.*, 1915, **94**, 241; from *J. Amer. Pharm. Assoc.*, 1914, **1**, 677).—*Struxine*, $C_{21}H_{30}O_4N_2$, colourless crystals, decomposing about 250°, has been obtained in about 0·1% yield from a few samples of beans from Cochin-China, which were insect-eaten and partly decomposed by prolonged exposure on wet fields. It is precipitated when the acid solution of the crude alkaloidal sulphates of nux vomica is just neutralised or is still faintly acid, whilst strychnine and brucine still remain in the solution as sulphates. The new alkaloid is regarded as a product of the decomposition, by fermentation or oxidation, of strychnine or brucine. It responds to the usual alkaloidal tests, is only very slightly bitter, and forms normal and acid salts; the *sulphate*, *hydrogen sulphate*, *hydrochloride*, *hydrobromide*, and *hydrogen tartrate* have been prepared. C. S.

Action of Pyridine on Certain Organic Sulphur and Selenium Compounds. II. M. RAFFO and G. ROSSI (*Gazzetta*, 1915, **45**, i, 28—34. Compare A., 1914, i, 572).—The action of pyridine on further sulphur compounds and on various selenium compounds has been investigated.

When a pyridine solution of thiophenol is boiled, the principal reaction consists in the formation of phenyl disulphide, evolution of hydrogen sulphide indicating that secondary reactions also occur.

When a pyridine solution of thiobenzanilide is boiled until liberation of hydrogen sulphide ceases, the compound, m. p. 202°, to which Jamieson ascribed the structure NPh:CPh·NPh·CSPh (A., 1904, i, 396) is obtained. The authors consider it more probable that this compound has the constitution NPh:CPh·S·CPh:NPh.

Similarly, phenylallylthiocarbamide yields hydrogen sulphide, allylthiocarbimide and *N*-phenylpropylene-ψ-thiocarbamide,



(compare Prager, A., 1890, 159).

Under similar conditions, diphenylseleniocarbamide decomposes principally into hydrogen selenide and carbodiphenylimide, the latter being converted by the water of the moist pyridine into carbanilide; the other products formed are aniline and triphenylguanidine, this probably resulting from the interaction of aniline and carbodiphenylimide. T. H. P.

Syntheses in the Diphenylmethane Series. LAMBERT THORP and E. A. WILDMAN (*J. Amer. Chem. Soc.*, 1915, **37**, 372—377).—This investigation was undertaken in the hope of effecting the synthesis of fluorene by the action of metals on 2 : 2′-dibromodiphenylmethane.

3 : 3′-*Diacetylaminodiphenylmethane*, m. p. 193°, forms colourless leaflets. When a solution of this substance in glacial acetic acid is treated with bromine, 6 : 6′-*dibromo*-3 : 3′-*diacetylaminodiphenylmethane*,

m. p. 284°, is produced which crystallises in small, colourless plates, and on hydrolysis with hydrochloric acid is converted into 6 : 6′-*dibromo*-3 : 3′-*diaminodiphenylmethane*, m. p. 114°. The latter compound is somewhat unstable and becomes brown on exposure to the air; its *hydrochloride* and *sulphate* were prepared.

2 : 2′-*Dibromodiphenylmethane* was obtained by the diazotisation of 6 : 6′-dibromo-3 : 3′-diaminodiphenylmethane as a colourless liquid with b. p. 234—235°/40 mm., n_D^{20} 1·6300, and D_4^{20} 1·6197. Attempts to induce this substance to undergo condensation with ring formation were not successful. Although it was treated with sodium in ether and in boiling xylene, and subjected to the action of copper bronze at 260° and of magnesium at the same temperature, it was in all cases recovered unchanged.

On heating a solution of 2 : 2′-dibromodiphenylmethane in glacial acetic acid with chromic acid, 2 : 2′-*dibromobenzophenone*, m. p. 86°, is produced which forms hexagonal plates; attempts were made to prepare its oxime and semicarbazone, but without success. E. G.

Antipyrine Methylarsinate. L. Barthe (*Pharm. J.*, 1915, **95**, 99; from *Bull. Soc. Pharm. Bordeaux*, 1914, 348).—Antipyrine methylarsinate, $AsOMe(OH)_2,2C_{11}H_{12}ON_2,4H_2O$, is obtained by boiling together 1 mol. of methylarsinic acid and 2 mols. of antipyrine in alcoholic solution, filtering, and leaving the solution to crystallise over sulphuric acid. The substance is soluble in alcohol and in water; at 20°, 100 parts of water dissolve 28·5 grams. It is not optically active. Its aqueous solution yields a white precipitate with sodium or potassium hydroxide, but not with ammonia, a red coloration with nitric acid, a fluorescence with copper sulphate, a greenish-blue coloration with nitrous acid, and a blood-red coloration with ferric chloride; alkaloidal reagents yield precipitates, and an odour like that of bitter almonds is produced when the substance is treated with sodium hypochlorite. Mercurous nitrate, added to the aqueous solution, gives a blackish precipitate, and not yellow as with antipyrine.

W. P. S.

Antipyrine Cacodylate. L. Barthe (*Pharm. J.*, 1915, **94**, 99; from *Bull. Soc. Pharm. Bordeaux*, 1914, 353).—Antipyrine cacodylate, $AsOMe_2{\cdot}OH,C_{11}H_{12}ON_2,2H_2O$, m. p. below 100°, is prepared by adding 1 mol. of antipyrine dissolved in dilute alcohol to a concentrated alcoholic solution of 1 mol. of cacodylic acid, boiling the mixture, and leaving it to crystallise over sulphuric acid. The substance is soluble (24·5%) in water and in alcohol. Its aqueous solution yields a white precipitate when treated with potassium or sodium hydroxide, but not with ammonia; copper sulphate solution produces a slight fluorescence, but no precipitate. Nitrous acid (sodium nitrite and acetic acid) gives a blue coloration, ferric chloride a blood-red colour, whilst the usual alkaloidal reagents all give precipitates. An odour like that of bitter almonds is produced when an aqueous solution of antipyrine cacodylate is treated with sodium hypochlorite.

W. P. S.

Hydantoins. XXIX. Geometrical Isomerism in the Hydantoin Series. TREAT B. JOHNSON and SIDNEY E. HADLEY (*J. Amer. Chem. Soc.* 1915, **37**, 171—177).—An account is given of the first case of geometrical isomerism observed in the hydantoin series.

When 2-thio-1 : 3-diphenylhydantoin is prepared by heating ethyl phenylaminoacetate with phenylthiocarbimide (Wheeler and Brautlecht, A., 1911, i, 501), a secondary product is obtained, m. p. 212°. By the condensation of benzaldehyde with 2-thio-1 : 3-diphenylhydantoin, the 4-benzylidene derivative, m. p. 197°, is produced, together with two other compounds, one of which appears to be a stereoisomeric modification of the hydantoin (m. p. 197°) whilst the other seems to be identical with the secondary product of the reaction between ethyl phenylaminoacetate and phenylthiocarbimide. On reducing 2-thio-1 : 3-diphenyl-4-benzylidenehydantoin with hydriodic acid, 2-thio-1 : 3-diphenyl-4-benzylhydantoin (Johnson and Shepard, A., 1914, i, 1091) is produced.

When 2-thio-1 : 3-diphenyl-4-benzylidenehydantoin is digested with chloroacetic acid, it yields two stereoisomeric forms of 1 : 3-*diphenyl*-4-*benzylidenehydantoin*, $NPh<^{CO\cdot NPh}_{CO\cdot C:CHPh}$. The *trans*-modification, m. p. 192°, crystallises in pale yellow, tetrahedral prisms, and the *cis*-form, m. p. 152°, forms rosettes of prisms. These two compounds can also be obtained by the condensation of 1 : 3-diphenylhydantoin with benzaldehyde. On reduction with hydriodic acid, both forms are converted into 1 : 3-diphenyl-4-benzylhydantoin (Johnson and Shepard, *loc. cit.*). E. G.

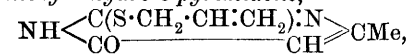
Hydantoins. XXX. Stereoisomeric Modifications of Benzylidenehydantoin. TREAT B. JOHNSON and JOSEPH S. BATES (*J. Amer. Chem. Soc.*, 1915, **37**, 383—385).—Johnson and Hadley (preceding abstract) have shown that the condensation products of disubstituted hydantoins with aldehydes are capable of existing in isomeric modifications. It has now been found that benzylidenehydantoin, $NH<^{CO\cdot NH}_{CO\cdot C:CHPh}$, also occurs in two modifications.

The ordinary form of benzylidenehydantoin, m. p. 220° (Ruhemann and Stapleton, T., 1900, **77**, 246), is the *cis*-modification. From the alcoholic mother liquor from which the substance had separated, a small quantity of the *trans*-modification, m. p. 246°, has been isolated, which crystallises in aggregates of distorted prisms; the yield is less than 1% of the theoretical. E. G.

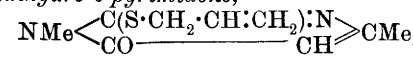
Pyrimidines. LXXIII. Alkylation of 2-Thiolpyrimidines. TREAT B. JOHNSON and HOWARD W. HAGGARD (*J. Amer. Chem. Soc.*, 1915, **37**, 177—183).—The earlier papers on the alkylation of 2-thiol-6-pyrimidones have dealt with the results obtained with compounds in which the thiol group contained a saturated alkyl radicle and, with one exception, all such thiol groups have been found to favour substitution in the 1- and 3-positions of the pyrimidine ring. A study has now been made of the alkylation of 2-allylthiol-4-methyl-

dihydro-6-pyrimidone and, in this case, no substitution in the 3-position has been observed.

2-*Allylthiol*-4-*methyldihydro*-6-*pyrimidone*,

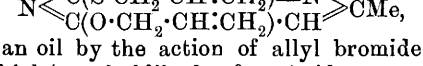


m. p. 131°, prepared by the action of allyl bromide on the sodium salt of 2-thio-4-methyluracil, forms colourless needles. When treated with methyl iodide and sodium ethoxide, it yields 2-*allylthiol*-1 : 4-*dimethyldihydro*-6-*pyrimidone*,



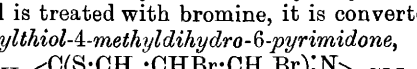
m. p. 43°, which crystallises in hexagonal tables, and is hydrolysed by hydrochloric acid with formation of 1 : 4-dimethyluracil.

6-*Allyloxy*-2-*allylthiol*-4-*methylpyrimidine*,



was obtained as an oil by the action of allyl bromide on the sodium salt of 2-allylthiol-4-methyldihydro-6-pyrimidone; on hydrolysis, it furnished 4-methyluracil.

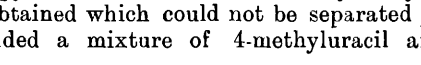
When a solution of 2-allylthiol-4-methyldihydro-6-pyrimidone in glacial acetic acid is treated with bromine, it is converted into 5-*bromo*-2-*βγ-dibromopropylthiol*-4-*methyldihydro*-6-*pyrimidone*,



m. p. 160—165° (decomp.), which crystallises in rosettes of needles.

By the action of ethyl bromide on the sodium salt of 2-allylthiol-4-methyldihydro-6-pyrimidone, a mixture of 2-allylthiol-4-methyl-1-ethyldihydro-6-pyrimidone and 6-ethoxy-2-allylthiol-4-methylpyrimidine was obtained which could not be separated; on hydrolysis the product yielded a mixture of 4-methyluracil and 4-methyl-1-ethyluracil.

Benzyl chloride reacted with the sodium salt of 2-allylthiol-4-methyldihydro-6-pyrimidone with formation of a mixture of 6-benzyloxy-2-allylthiol-4-methylpyrimidine and 2-allylthiol-1-benzyl-4-methyldihydro-6-pyrimidone which on hydrolysis furnished 4-methyluracil and 1-benzyl-4-methyluracil.

When the sodium salt of 2-methylthiol-4-methyldihydro-6-pyrimidone is treated with allyl bromide, 6-*allyloxy*-2-*methylthiol*-4-*methylpyrimidine*,  , b. p. 160—164°/17 mm., is obtained as a yellow oil; on hydrolysis it is converted into 4-methyluracil. E. G.

Pyrimidines. LXXIV. Synthesis of 4-Phenylcytosine. Treat B. Johnson and E. Heaton Hemingway (*J. Amer. Chem. Soc.*, 1915, **37**, 378—383).—Johnson and Hill (A., 1914, i, 879) have shown that 4-phenyl*iso*cytosine exists in four isomeric modifications. With a view to elucidating the nature of this isomerism, a study has now been made of 4-phenylcytosine, and it has been found that this compound exists in two distinct forms.

2-Thio-4-phenyluracil can be readily obtained in a yield of about

73·3% of the theoretical by heating an alcoholic solution of thiocarbamide with ethyl benzoylacetate in presence of sodium ethoxide; when digested with chloroacetic acid, it is converted quantitatively into 4-phenyluracil (Wheeler and Merriam, A., 1903, i, 525).

2-*Ethylthiol*-4-*phenyldihydro*-6-*pyrimidone*,

$$NH\begin{matrix}<C(SEt):N\\CO—CH\end{matrix}>CPh,$$

m. p. 226°, obtained in 78% yield by the action of ethyl bromide on the sodium salt of 2-thio-4-phenyluracil, crystallises in needles; it is converted by phosphoryl chloride into 6-*chloro*-2-*ethylthiol*-4-*phenylpyrimidine*, $N\begin{matrix}<C(SEt):N\\CCl—CH\end{matrix}>CPh$, b. p. 232°/26·5 mm., which gives a quantitative yield of 4-phenyluracil on hydrolysis with hydrochloric acid. When this chloropyrimidine is heated with alcoholic ammonia at 130—135°, 6-*amino*-2-*ethylthiol*-4-*phenylpyrimidine*,

$$N\begin{matrix}<C(SEt)=N\\C(NH_2)\cdot CH\end{matrix}>CPh,$$

m. p. 120°, is produced, which crystallises in thin plates. On hydrolysing this compound with hydrobromic acid, it is converted into 4-*phenylcytosine*, $N\begin{matrix}<CO——NH\\C(NH_2)\cdot CH\end{matrix}>CPh,H_2O$; the *hydrobromide* and *hydrochloride* both crystallise in long needles with $1H_2O$; the former does not melt below 300° and the latter has m. p. 274° (decomp.); the *nitrate* crystallises in either needles or prisms and decomposes above 245°. 4-Phenylcytosine, when first prepared, crystallises in rosettes of needles, but when recrystallised from boiling absolute alcohol, it is obtained in the form of rhombohedral prisms. On crystallisation from 95% alcohol, a mixture of both needles and prisms is obtained. Neither modification gives a definite melting or decomposition point.

E. G.

5-Keto-1-phenyl-4 : 5-dihydrotriazole-3-sulphinic Acid and 5-Keto-1-phenyl-4 : 5-dihydrotriazole-3-methylsulphone. E. W. Esslinger and S. F. Acree (*J. Amer. Chem. Soc.*, 1915, **37**, 183—189).—Earlier work has shown that 1-phenyl-3-thiourazole yields only one mono-alkyl derivative on alkylation by various methods (A., 1903, i, 867) whereas 1-phenylurazole yields a mixture of the 2-N- and 3-O-derivatives. These facts can be explained on the assumption that urazole salts exist in two tautomeric forms (A., 1908, i, 919; 1910, i, 520). When the alkyl derivatives of 3-thio-1-phenylurazole are heated with acids at 125° under pressure, an alkylmercaptan is produced, indicating that the alkyl group is attached to the sulphur atom.

Experiments have now been carried out which show that on oxidation 1-phenyl-3-thiourazole yields very soluble sulphinic and sulphonic acids whilst its alkyl derivatives furnish insoluble sulphone-like substances. The conclusion is therefore drawn that these alkyl derivatives have an alkyl group attached to the sulphur atom and not to the nitrogen atom, and that 3-thio-1-phenylurazole is alkylated in the tautomeric thio-enol forms, $\begin{matrix}NPh—N\\|\\CO\cdot NH\end{matrix}>C\cdot SH$, and $\begin{matrix}NPh—N\\|\\C(OH):N\end{matrix}>C\cdot SH$.

5-*Keto*-1-*phenyl*-4 : 5-*dihydrotriazole*-3-*sulphinic acid*,

$$\begin{matrix}\mathrm{NPh{-}N}\\ |\\ \mathrm{CO{\cdot}NH}\end{matrix}\!\!>\!\mathrm{C{\cdot}SO_2H},$$

m. p. 174—178°, obtained by oxidising the sodium salt of 1-phenyl-3-thiourazole with alkaline solution of potassium permanganate or with 30% hydrogen peroxide, yields a *disilver* salt,

$$\begin{matrix}\mathrm{NPh{-\!-\!-}N}\\ |\\ \mathrm{C(OAg){:}N}\end{matrix}\!\!>\!\mathrm{C{\cdot}SO_2Ag,H_2O}.$$

5-*Keto*-1-*phenyl*-4 : 5-*dihydrotriazole*-3-*methylsulphone*,

$$\begin{matrix}\mathrm{NPh{-}N}\\ |\\ \mathrm{CO{\cdot}NH}\end{matrix}\!\!>\!\mathrm{C{\cdot}SO_2Me},$$

m. p. 206—207°, formed by the oxidation of 3-thio-1-phenylmethylurazole, furnishes a *silver* salt, $\begin{matrix}\mathrm{NPh{-\!-\!-}N}\\ |\\ \mathrm{C(OAg){:}N}\end{matrix}\!\!>\!\mathrm{C{\cdot}SO_2Me}$. On treating the sodium salt of the sulphone with methyl iodide, it yields about 40% of 5-*keto*-1-*phenyl*-4-*methyl*-4 : 5-*dihydrotriazole*-3-*methylsulphone*, $\begin{matrix}\mathrm{NPh{-\!-\!-}N}\\ |\\ \mathrm{CO{\cdot}NMe}\end{matrix}\!\!>\!\mathrm{C{\cdot}SO_2Me}$, m. p. 94—95°, together with 60% of 5-methoxy-1-phenyl-4 : 5-dihydrotriazole-3-methylsulphone.

5-*Keto*-1-*phenyl*-4 : 5-*dihydrotriazole*-3-*ethylsulphone* has m. p. 199·5—200° and yields a stable *silver* salt. By the action of ethyl iodide on the sodium salt of this sulphone, 5-*keto*-1-*phenyl*-4-*ethyl*-4 : 5-*dihydrotriazole*-3-*ethylsulphone*, m. p. 74—75°, is obtained; the ratio of this ketonic substance to the enolic compound formed simultaneously was 40 : 60. E. G.

Precipitation of Serum-Albumin and Gelatin by Alkaloidal Reagents. Paul J. Hanzlik (*J. Biol. Chem.*, 1915, **20**, 13—24).—For the alkaloidal reagents, a certain amount of free acid is necessary for the formation of complex insoluble compounds. For dialysed horse-serum and gelatin, the mechanism of precipitation by tannin is different. It behaves like certain alcohols (phenol, resorcinol, etc.), since the maximum of precipitation occurs at the *iso*-electric point. The precipitation in the case of serum is not influenced by wide differences of concentration nor by the addition of such neutral salts as chloride and thiocyanate. W. D. H.

Simpler Nucleotides from Yeast-Nucleic Acid. Walter Jones and A. E. Richards (*J. Biol. Chem.*, 1915, **20**, 25—35).—Levene and Jacobs showed that yeast-nucleic acid, a tetranucleotide, can be split into its four component mononucleotides by boiling with mineral acids; the two which contain pyrimidine bases are not further broken up. In a mixed nucleotide, the separation of purine and pyrimidine bases is no longer necessary, but an estimation of the liberated phosphoric acid gives a measure of the amount of both present. In enzymatic hydrolysis, the first cleavage is into two dinucleotides, one containing guanine and cytosine, the other adenine and uracil. Thannhauser has also described a tri-nucleotide obtained by the digestive action of duodenal juice; in this uracil is lacking. In the present paper, the two dinucleotides and guanylic acid are discussed.

As the tissue enzymes are so numerous which act on nucleic acid, and the factors complex which influence the reaction, full details are given of the precautions to be adopted in the method of preparing the dinucleotides by the action of pancreas on yeast-nucleic acid. Analyses and some constants are also given. A method is also described for preparing guanylic acid from guanosine obtained by the action of fresh pancreas extract on yeast-nucleic acid. The interesting suggestion is made that when guanylic acid is found in animal tissues, it comes from vegetable food. W. D. H.

Fibrin. A. W. Bosworth (*J. Biol. Chem.*, 1915, **20**, 91—94).—Fibrin combines with four equivalents of base to form a compound neutral to phenolphthalein. It also forms acid salts with one, two, and three equivalents of base; all the combinations with sodium, potassium, and ammonium are soluble. The calcium fibrinates containing one and two equivalents are insoluble; those with three and four equivalents are soluble. Fibrin combined with one equivalent of acid is insoluble, and with more than one, soluble. Fibrin, unlike caseinogen, is not strong enough as an acid to decompose calcium carbonate. The molecular weight of fibrin is given as 6666. Carbon dioxide precipitates fibrin from a solution of calcium fibrinate, but not from solutions of sodium, potassium, or ammonium fibrinate. W. D. H.

Influence of Certain Capillary-active Substances on Enzyme Activity. George H. Chapman (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 293—337).—The author has investigated the action of alcohols, esters, ketones, and other substances which readily alter the surface tension of solutions, on invertase, pepsin, trypsin, catalase and lipase. A general relation between concentration of the capillary-active substance, the surface tension and the rate of enzyme action could not be discovered in the case of any of these enzymes.

In the presence of sucrose, the inhibitory action of the capillary-active substances on invertase was very much reduced. Neither sucrose nor Witte's peptone had a similar protective influence on pepsin except against the lower alcohols. H. W. B.

Studies on Enzyme Action. XII. Esterase and Lipase of Castor Beans. K. George Falk and K. Sugiura (*J. Amer. Chem. Soc.*, 1915, **37**, 217—230).—In an earlier paper (A., 1914, i, 98) it was shown that castor beans appear to contain two enzymes, one of which is soluble in water and is more active towards ethyl butyrate than towards glyceryl triacetate, whilst the other is insoluble, and is more active towards glyceryl triacetate than towards ethyl butyrate. For convenience, the former is referred to as esterase and the latter as lipase.

The effect of sodium chloride and sodium sulphate solutions on the activity of these enzymes has been studied. It has been found that the action of the esterase is inhibited by sodium chloride at all concentrations, whilst that of the lipase is accelerated at some concentrations, and inhibited at certain higher concentrations. Sodium sulphate does not affect the activity of the castor bean preparation towards

ethyl butyrate, but causes a marked acceleration of its action on glyceryl triacetate.

The activity of the castor bean preparation is not affected by desiccation in a vacuum in presence of calcium chloride or phosphoric oxide, but it is greatly decreased when the material is heated at 100—110°.

An esterase preparation was separated by extraction with water and its properties were studied both in solution and in the solid state; it is suggested that this enzyme is probably identical with glycerophosphatase. A lipase preparation, extracted with 1·5 *N*-sodium chloride was also investigated. It is shown that both the esterase and lipase are essentially of a protein character. E. G.

Physiological Chemistry.

History and Development of Physico-chemical Research in Biology. H. J. HAMBURGER (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 6—27).—Historical. H. W. B.

Internal Friction and Surface Tension in Biological Processes. I. TRAUBE (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 275—291. Compare Schryver, A., 1911, i, 245).—The author points out that Schryver's assumption of a limiting layer between the two phases of a heterogeneous system is of great significance in the interpretation of the most varied, biological velocity-processes (hæmolysis, ferment destruction, narcosis, osmosis, etc.). The viscosity and surface tension of such a limiting layer will modify the hæmolytic power of lipoid-soluble substances (Traube, A., 1908, ii, 708), for the greater the viscosity the greater the resistance to the entrance of the hæmolytic fluid, and the greater the difference in surface tension required to bring about hæmolysis.

The viscosities of various sera have been measured by the author, and it is found that the serum of the guinea-pig, which has the lowest viscosity, has the greatest content of "complement." The alteration in surface tension and the content of complement of sera appear to run parallel.

The relation between the inhibitory influence of certain narcotics on clot formation and their surface tension (Schryver, A., 1914, i, 616) probably becomes an absolute one when the effect of the viscosity of the limiting layer is taken into account.

An osmotic law of the nature of Ohm's law is formulated in the terms that the osmotic velocity of a substance (the quantity of material osmotically moved in a unit of time) is proportional to the cohesion or surface pressure, and inversely proportional to the viscosity constant. H. W. B.

Changes in the Blood After Muscular Activity and During Training. EDWARD C. SCHNEIDER and LEON C. HAVENS (*Amer. J. Physiol.*, 1915, **36**, 239—259).—During rest a quantity of blood is stagnant in the splanchnic area. On exertion, carbon dioxide is produced, which stimulates the adrenal gland; the increased output of adrenaline forces the stagnant blood into the general circulation; this increases the specific gravity, hæmoglobin, and corpuscular content of the blood. Muscular contraction accelerates also the flow of lymph, and lymph rich in leucocytes is thrown into the blood. Figures are given to support these general conclusions. Abdominal massage corrects stagnation of blood there. At a great altitude exercise does not have these effects except in so far as a rise in white corpuscles and platelets is seen. During athletic training the red corpuscles and hæmoglobin increase; leucocytes and platelets do not alter. Mononuclear cells increase 4%. No change in total oxygen capacity or total blood volume occurs.

W. D. H.

The Effects of Thyroid Extracts on Blood Pressure. G. C. FAWCETT, JOHN ROGERS, JESSE M. RABE, and S. P. BEEBE (*Amer. J. Physiol.*, 1915, **36**, 113—125).—Iodine was present in all the fractions used, but those richest in iodine (coagulable fractions) produce little or no fall of blood pressure; the residue after the removal of the coagulable fractions has a depressor effect after intravenous but not after subcutaneous injection; rapidity of the heart is sometimes also produced. The active substance is not precipitated by basic lead acetate, is unaffected by boiling or by passage through a Berkefeld filter, and is soluble in alcohol. No immunity was observed during the limit of the experiments (four to six hours). W. D. H.

The Influence of Blood Transfusion on the Kidneys. I. A. RABENS (*Amer. J. Physiol.*, 1915, **36**, 294—298).—The transfusion of blood has no effect on the kidneys (as Hedon considers), nor on the body metabolism generally. W. D. H.

Factors Affecting the Coagulation Time of Blood. VI. The Effect of Rapid Progressive Hæmorrhage. KATHERINE R. DRINKER and CECIL K. DRINKER (*Amer. J. Physiol.*, 1915, **36**, 305—324).—Rapid progressive hæmorrhage produces progressive lessening in the coagulation-time of blood. An occasional animal shows no change. Antithrombin is lessened when the coagulation-time decreases, and remains constant when it does not. Prothrombin tends to increase slightly at first and then decreases slightly. Fibrinogen estimated as a heat-coagulum decreases as hæmorrhage progresses. The blood-platelets show no alteration. W. D. H.

The Blood Relationship of Animals as Displayed in the Composition of the Serum-Proteins. III. A Comparison of the Sera of the Hen, Turkey, Duck, and Goose with respect to their Content of Various Proteins. W. B. THOMPSON (*J. Biol. Chem.*, 1915, **20**, 1—6).—Brailsford Robertson's refractometric

method was employed for the estimations; the birds were kept fasting between eighteen and twenty hours before they were bled. The following table summarises the average results obtained:

	Total proteins per cent. of serum.	Insoluble globulin	Total globulins	Total albumins
		per cent. of the total proteins.		
Hen	5·0	14·9	23	77
Rooster	6·0	11·4	19	81
Turkey	6·2	7·4	16	84
Duck	6·7	21·6	29	72
Goose	4·1	17·2	26	74

W. D. H.

The Blood Relationship of Animals as Displayed in the Composition of the Serum-Proteins. IV. A Comparison of the Sera of the Pigeon, Rooster, and Guinea Fowl with respect to their Content of Various Proteins in the Normal and in the Fasting Condition. R. S. Briggs (*J. Biol. Chem.*, 1915, **20**, 7—11).—This investigation was carried out by the same method as in the preceding paper, and the following table gives the results:

	Total proteins per cent. of serum.	Insoluble globulin	Total globulins	Total albumins
		per cent of the total proteins.		
Pigeon, normal	4·4	7·3	28	72
,, fasting	4·8	2·7	14	86
Rooster, normal	3·3	16·4	38	62
,, fasting	4·1	12·1	33	68
Guinea-fowl normal	3·7	6·2	30	70
,, fasting	4·1	4·7	5	95

W. D. H.

Physico-chemical Researches on Blood Sera. I. Traube (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 389—411).—The author has determined the following constants for a large number of human and animal sera: (*a*) viscosity, (*b*) surface tension, (*c*) alkalinity, and (*d*) quantity of capillary-active acids. The first two constants have been measured by the viscostagonometer (A., 1912, ii, 832) and the last two by the stalagmometer.

The new method of estimating the alkalinity is based on the observation that the surface tension of solutions of many alkaloids is lowered by the addition of a trace of alkali. Applying this method to the blood it is found that human blood serum has an alkalinity corresponding with a 0·05—0·06*N*-potassium hydroxide solution.

The method for the estimation of the capillary-active acids in serum depends on the fact that strong mineral acids liberate them from the serum.

Of all the animal sera examined, that of the guinea-pig (which contains the largest quantity of "complement") possesses the smallest viscosity, the least alkalinity, and the smallest amount of

capillary-active acids. The alkalinity of the sera of birds is greater than that of mammals, whilst the serum of the frog has the least alkalinity of all.

The results of the examination of human sera were most distinctive in the cases of the viscosity constant and the surface tension. The viscosity constant is considerably increased in jaundice, heart disease, etc., and lowered in anæmia, etc. The alkalinity of human serum is lowered in all cachectic diseases—carcinoma, pernicious anæmia, pneumonia, etc. H. W. B.

Capillarimetric Researches on the Serum and Cerebrospinal Fluid of Man. Bruno Kisch and Otto Remertz (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 354—388).—The surface tension of human blood serum, in health and in many diseased conditions, is exceedingly constant provided the specimen is clear and not discoloured with hæmoglobin. Chylous sera and those tinged red with hæmoglobin have a distinctly lower surface tension. The chief instances in which the surface tension was constantly lower than normal were obtained in cases of epilepsy, eclampsia, uræmia, and jaundice.

Inactivation of sera by warming at 56—60° for half-an-hour lowers the surface tension, due, apparently, to an alteration in the condition of the serum colloids. After having once been inactivated, repeated warming and cooling of the serum does not change the surface tension.

Serum from fœtal blood has a distinctly lower surface tension than that from the mother, and it becomes still lower when inactivated at 56°. This is possibly due to the presence of capillary-active substances in the fœtal blood or to a difference in the composition of its colloid constituents. Throughout pregnancy, the blood serum remains normal with respect to its surface tension and behaviour on inactivation.

The cerebrospinal fluid also has a remarkably constant surface tension which is always considerably higher than that of the blood serum. Any alteration in the latter is usually accompanied by a corresponding alteration in the former.

Age and sex have no influence on the surface tension of either the blood serum or the cerebrospinal fluid. H. W. B.

Hæmolysis. I. Hæmolysis by Capillary-active Substances in Cold-blooded Animals. Bruno Kisch (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 60—81).—The author has ascertained the concentration and surface tension of the solutions of a series of capillary-active substances (methyl, ethyl, propyl, *iso*butyl and *iso*amyl alcohols, acetone, and ethyl ether), which just hæmolyse the erythrocytes of certain cold-blooded animals (*Sipunculus nudus*, *Scyllium catulus*, *Torpedo marmorata*, *Scorpena scropha*, *Lophius piscatorius*, *Labrus tardus*, and *L. festivus*). It is found that hæmolysis is not accomplished by iso-capillary solutions, and consequently some other factor besides surface tension and lipoid-solubility is concerned in the hæmolytic process. The subjects of experiment

are enumerated above in the order corresponding usually with the relative ease with which their erythrocytes are hæmolysed by the alcohols employed, *Sipunculus* requiring the lowest concentration of the alcohol and *Labrus* the highest. H. W. B.

Lipoids in Immunity. II. F. H. THIELE and DENNIS EMBLETON (*J. Path. Bact.*, 1915, **19**, 349—371).—The hæmolytic power of serum is not related to its lipolytic activity. Hæmolysin is not lipase. Anti-substances cannot be provoked against tissue fats, lipoids, or phosphatides. The phosphatides of the tubercle bacillus, however, provoke the formation of anti-substances, which are not wholly specific. Anaphylaxis was also noted. W. D. H.

The Mechanism of Anti-substance Action. F. H. THIELE and DENNIS EMBLETON (*J. Path. Bact.*, 1915, **19**, 372—391).—The activity of complement depends on its concentration, not on its amount. Amboceptor combines quantitatively with its antigen, and its activity does not depend on its concentration. The curves of complement action resembles those of enzyme action. W. D. H.

Physico-chemical Behaviour of Ferments in the Stomach After Administration by the Mouth. Nature of Proferments. ERNST PŘIBRAM and A. PERUTZ (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 269—274).—When rennet or pepsin is introduced into the rabbit's stomach it is quickly adsorbed, and if the animal is killed from thirty minutes to an hour after feeding, the adsorbed ferment can be extracted from the mucous membrane by means of sodium carbonate solution. On acidifying the extract, the active enzymes are set free. The mucous membrane of the normal rabbit's stomach, when similarly treated, yields neither pepsin nor rennet.

Trypsin in alkaline solution is also rapidly adsorbed by the living mucous membrane of the stomach, and can be subsequently extracted by dilute acid and shown to be active by its behaviour towards protein in the presence of alkali. These adsorbed ferments stand in the same position as the so-called "proferments" or "zymogens," and yield the active enzymes by exactly similar treatment.

The authors also found that when the enzymes were administered in a 10% sucrose solution the adsorption phenomena did not occur, the enzymes (pepsin and rennet) meanwhile retaining their activity unchanged. H. W. B.

Quantitative Relation between Temperature and Standard Metabolism in Animals. AUGUST KROGH (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 491—508).—The effect of varying the temperature of animals on the metabolism (as measured by the oxygen output) has been determined under conditions involving the minimum functional activity, that is, the nearest attainable approximation to the basal metabolism which would obtain when all organs were absolutely at rest. Under these standard conditions

(all nervous influences being abolished by curare and methyl carbamate) the influence of temperature on the metabolism of an animal is regular and constant, and can be expressed in a definite curve which is not a straight line and cannot be expressed by Arrhenius' formula or van't Hoff's rule indicating the temperature relations of chemical reactions.

The curves obtained for frogs and goldfish and, in a single experiment, for a young dog are identical, while that for chrysalides of *Tenebrio* is distinctly different, although of the same general type. H. W. B.

Nature and Formation of the Fertilisation Membrane of the Echinoderm Egg. J. F. McClendon (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 163—168).—If the mucus layer (jelly, chorion, zona pellucida) is removed from the sea-urchin's egg before fertilisation, a fertilisation membrane is not formed, although the egg segments. The author was also unable to detect the presence of any membrane of the toughness that characterises the fully-developed fertilisation membrane on the surface of the unfertilised egg. These observations confirm the author's view that the fertilisation membrane is formed by the mutual precipitation, at their surface of contact, of two oppositely charged colloids—the mucus and the perivitelline jelly. H. W. B.

Parallelism between Increase in Permeability and Abnormal Development of Fish Eggs. J. F. McClendon (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 28—34. Compare A., 1912, ii, 1196).—Distilled or sea-water solutions of nicotine or the salts of lithium, sodium, potassium, calcium, or magnesium all produce abnormalities in the development of the eggs of the smelt or of *Fundulus heteroclitus* placed in them in early segmentation stages. These substances are found to increase the permeability of the eggs to salts or their ions, the eggs being normally impermeable to salts in pure water or "balanced" salt solutions. Since the increase in permeability occurs before the abnormalities appear, it is probable that the abnormal permeability is the cause of the structural abnormality. H. W. B.

Antagonistic Action of Carbon Dioxide and Adrenaline on the Heart. S. W. Patterson (*Proc. Roy. Soc.*, 1915, [*B*], **88**, 371—396).—The author has investigated the action of carbon dioxide and adrenaline on the heart isolated from the nervous system by Starling and Knowlton's method (A., 1912, ii, 571), the animals employed being dogs and cats.

It is found that carbon dioxide in all doses appears to have a depressant action on all the functions of the heart; the contractile stress is developed more slowly, and the output of blood is diminished. The coronary circulation is unaltered.

Adrenaline increases the rate of contraction of the heart and the rate of development of the contractile stress. It seems to have a specific action in mobilising the "contractile substance" and

increasing the energy changes taking place at the surface of the muscle fibres during contraction. The result is that the ventricle contracts violently, and the blood is expelled under great pressure into the aorta. The coronary circulation is greatly increased, and the nutrition of the heart improved. Relaxation takes place rapidly, but the onset of the next systole comes so early that the filling of the heart, and consequently the output of blood per beat, are less than normal, although the total output of the ventricle per minute may be equal to or greater than normal.

By combining carbon dioxide with adrenaline in proper ascertained doses, greater rate of contraction and relaxation may be obtained, together with a lengthening of the whole diastolic period. There is thus time for greater filling, and therefore increased output of blood per beat and per minute. The coronary output is also increased, and the slower contraction of the heart is more effective in driving the blood into the aorta. The combined action of carbon dioxide and adrenaline in conditions such as accompany short but severe muscular exercise enables the heart to respond quickly, and furnish the maximum output of blood. H. W. B.

The Influence of Oxalates, Citrates, and Tartrates on the Isolated Heart. William Salant and Selig Hecht (*Amer. J. Physiol.*, 1915, **36**, 126—144).—The order of toxicity is citrate, oxalate, tartrate. The effect does not support the view that the salts precipitate calcium, or lead to the formation of non-ionised calcium salts, since calcium citrate and tartrate can be utilised by the heart. The action is rapid, and the theory that the changes are due to penetration into the cells is rejected. The effects are due to extra-cellular changes. W. D. H.

Reflexes from the Intestinal Mucosa to the Stomach. E. H. Brunemeier and A. J. Carlson (*Amer. J. Physiol.*, 1915, **36**, 191—195).—Gastric juice, chyme, acids, alkalis, water, milk, and oil introduced into the small intestine in dogs inhibit gastric tonus, and gastric hunger contractions. This is due partly to mechanical, but mainly to chemical stimulation; the reflex path may be long (central) and short (by Auerbach's plexus).
W. D. H.

Presence of Histidine-like Substances in the Pituitary Gland (Posterior Lobe). T. B. Aldrich (*J. Amer. Chem. Soc.*, 1915, **37**, 203—208).—An examination of the desiccated, defatted, posterior lobe of the pituitary gland has been tested for histidine by Inouye's modification of Pauly's reaction (A., 1913, ii, 164). Although a positive reaction was obtained, it is probable that it was not due to histidine, since Fischer's modification of Weidel's reaction and Knoop's reaction with bromine both gave negative results. It therefore seems likely that the substance in the pituitary gland material was not histidine, but some compound or compounds related to histamine (β-aminoethylglyoxaline). These substances are probably present either in the free state or combined with something other than protein.

The results of this work indicate that Pauly's reaction is not specific for histidine unless other compounds, such as tyrosine, *p*-hydroxyphenylethylamine, β-amino-4-ethylglyoxaline, and adrenaline have been removed, but is rather a general reaction for a class of compounds. E. G.

Degree of Acidity of Muscle under Various Mechanical Conditions of Contraction. F. Porcelli-Titone (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 338—353).—The concentration of hydrogen ions in the muscle (frog's gastrocnemius) expressed in grams per litre increases from 16×10^{-8} in the resting condition to 61×10^{-8} after tetanisation until it just ceases to contract. When the muscle does work, the acidity rises still higher to 98×10^{-8} after two hundred contractions. Muscles contracting two hundred times under isometric conditions reached the corresponding figures 89×10^{-8}, and, under a constant load, to 44×10^{-8}. These results are regarded as confirming the hypothesis that the metabolism of the muscle varies according to the conditions under which it contracts. H. W. B.

Local Deposits of Cholesterol in the Tissues. Matthew J. Stewart (*J. Path. Bact.*, 1915, **19**, 305—314).—Crystalline cholesterol is deposited in the tissues in various pathological conditions; this induces a cellular reaction, in which numerous "foamy" endothelial cells, and giant cells probably of endothelial origin, made their appearance. W. D. H.

Action of Hydrogen Ions on the Phagocytosis of Carchesium lachmani. N. K. Koltzov (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 82—107. Compare A., 1913, i, 224).—The author has studied the influence of acids and acid-salts on the power of the infusoria *Carchesium lachmani* to ingest particles of Chinese ink. The phagocytic power is greatest when the infusoria are in neutral solutions, a slight excess of hydrogen or hydroxyl ions exerting a distinct inhibitory action. The reduction of the acidity of a medium by the addition of sodium citrate or phosphate enables phagocytosis to occur to a correspondingly greater extent. The reactivity of the infusoria to the slightest alteration in the acidity of the medium is so sharp as to lead the author to suggest that it may form the basis of a new method for the estimation of the concentration of hydrogen ions in a solution. H. W. B.

Experiments on the Nature of the Photogenic Substance in the Firefly. E. Newton Harvey (*J. Amer. Chem. Soc.*, 1915, **37**, 396—401).—Experiments on the firefly are described which show that the dried material can be extracted with ether, chloroform, cold ethyl alcohol, carbon tetrachloride, acetone, or toluene without impairing its phosphorescent power. Boiling ethyl alcohol, cold amyl alcohol, and ethyl butyrate destroy the light-producing material. The photogen is also destroyed when the tissue is extracted for an hour with oxygen-free water. The same result

was obtained on extraction with Ringer's solution, sea-water, 0·125*M*-sodium chloride, 0·05*M*- and 0·01*M*-sodium hydroxide, and 0·02*M*-hydrochloric acid. These results indicate that water, oxygen, and a photogenic substance are not the only factors involved in the production of light, and show that the photogen is very unstable. E. G.

Experiments on the Nature of the Photogenic Processes in the Lampyridæ. F. ALEX. MCDERMOTT (*J. Amer. Chem. Soc.*, 1915, **37**, 401—404).—Experiments have been made on the same lines as those described by Harvey (preceding abstract) with material prepared from *Photinus pyralis* and *P. castus*, and attempts have been made to obtain evidence of the breaking down of nucleic acid during the photogenic process, as suggested by Lund (*J. Exper. Zool.*, 1911, **11**, 415).

The results confirm those obtained by Harvey, showing that a phosphorescent substance cannot be extracted from the dry tissue by dilute acid or alkaline solutions even in the absence of oxygen, and also indicate that the deposits of purine substances which form the so-called reflecting layer of the photogenic organs of the *Lampyridæ* cannot be traced satisfactorily to the breaking down of nucleic acids. E. G.

The Body Surface of Flounders and its Relation to Gaseous Metabolism. SERGIUS MORGULIS (*Amer. J. Physiol.*, 1915, **36**, 207—216).—The surface of flounders is computed by the ordinary formula, $S = K\sqrt[3]{w^2}$, K being 13·44. The metabolic processes bear no direct relation either to the weight or surface of the flounder; the oxygen consumption diminishes per gram-hour, but increases per square centimetre-hour as the animals become larger. Removal of the fins reduces the surface by more than 30% without materially influencing the weight of the fish; this does not affect the oxygen consumption. Under these conditions the oxygen consumption is proportional to the mass. During fasting, K is higher than normal. W. D. H.

Fasting Flounders. SERGIUS MORGULIS (*J. Biol. Chem.*, 1915 **20**, 37—46).—Aquatic animals depend on particulate food, and live on their own tissues during fasting. Organic matter dissolved in sea-water plays no rôle in their nutrition. The absolute loss of protein is much greater than that of fat. In fish, nitrogenous metabolism is stated to be the principal source of energy. The average respiratory quotient during fasting in flounders is 0·76. W. D. H.

Absorption of Water through the Skin of a Frog. J. F. MCCLENDON (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 169—172).—The absorption of water through the skin of a live frog is found by the author to be greater in relation to the surface area than that through the skin of a pair of amputated legs. If the skin of one amputated leg is removed and filled with 0·7% sodium

chloride solution and then immersed, together with the other unskinned leg, in water, the amount of water absorbed in the first hour is the same in each case. The conclusion drawn by the author is that the absorption of water by a frog's leg is the result of the osmotic pressure of the fluids in and between the cells of the tissues.

Experiments also showed that the rate of osmosis through frog's skin is constant, whether the water is passing inwards or outwards.

H. W. B.

Permeability of Cells for Acids. E. Newton Harvey (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 463—478).—A pigment, antedonin, occurring in the epithelium of the viscera of the Prickly Fish, a holothurian, *Stichopus ananas*, has been used as an indicator for the penetration of acids. Living tissues are resistant to the penetration of all acids except salicylic, benzoic, and possibly valeric acids. The degree of resistance varies with the acid, and is not nearly so marked as in the case of alkalis. The rate of penetration of hydrochloric acid is roughly proportional to the concentration.

There is no relation between the degree of dissociation of an acid and its rate of penetration or between degree of dissociation and toxicity. It is found that acids which penetrate most readily are most toxic, irrespective of their strength.

A general relation exists between penetrability, lipoid solubility, and capillary activity; but it is not exact and not quantitative. The order of the acids arranged in accordance with penetrability is not in exact agreement with that for the lipoid solubility, or for lowering of surface tension, acetic, propionic, and butyric acids being most out of place.

Cells behave towards acids and alkalis as if they were droplets of fat or fat solvent. If an acid is soluble enough in fatty substances, it encounters no resistance at the cell surface; if it is insoluble in lipoids, or only slightly soluble, it appears as if the cell surface must be destroyed before it can enter. The strength of the acid and possibly also a specific action of the anion on the surface proteins then determine its rate of entrance, or, better, its rate of alteration of cell surface.

Dead cells are readily permeable to all acids. H. W. B.

The Effect of Pituitary Extract on the Secretion of Cerebrospinal Fluid (Choroidorrhœa). Lewis H. Weed and Harvey Cushing (*Amer. J. Physiol.*, 1915, **36**, 77—103).—Dixon and Halliburton (A., 1913, i, 1413) found no effect on the secretion of cerebrospinal fluid. The present authors obtained negative results with several preparations. These vary a good deal in the relative amounts of various active principles; but there was always a sufficiency of positive results to indicate that extracts of the posterior lobe increase the rate of secretion of the fluid. It is a true secretion of the choroid plexuses, and not a mere gush produced mechanically. The experiments were performed on dogs, the

cannula being inserted through the corpus callosum into the third ventricle. Volatile anæsthetics were used. W. D. H.

The Effect of Repeated Injections of Pituitrin on Milk Secretion. SUTHERLAND SIMPSON and R. L. HILL (*Amer. J. Physiol.*, 1915, **36**, 347—351).—The intravenous, intramuscular, or subcutaneous administration of pituitary extract to a lactating animal causes a marked increase in the amount and fat-content of the milk formed. But if the injection is continued for months in a goat, immunity is established. W. D. H.

Nature of the Deposit Obtained from Milk by Spinning in a Centrifuge. H. S. HALCRO WARDLAW (*J. Roy. Soc. New South Wales*, 1914, **48**, 152—171).—The deposit which is obtained when milk is subjected to centrifugal action has the following average composition: Caseinogen, 57%; other proteins, 16%; lactose, 16%; other non-nitrogenous organic substances, 3%; ash, 8%. The rate of deposition of the substance is not constant, at first decreasing and then increasing; the amount of ash shows a variation in the opposite direction to that of the rate of deposition. The ash contains 43·1% of CaO and 43·9% of P_2O_5. From 25% to 70% of the deposit is soluble in water, and about 90% of the ash is found in the soluble portion. The removal of the deposit does not lower the freezing point of the milk. W. P. S.

The Diffusible Phosphorus of Cow's Milk. H. S. HALCRO WARDLAW (*J. Roy. Soc. New South Wales*, 1914, **48**, 253—266).—When a large volume of milk is dialysed against a small volume of water, the freezing point of the dialysate after twenty-four hours approximates to that of the milk, and does not change as the dialysis is continued; a definite state of equilibrium is reached. The diffusible phosphorus of cow's milk amounts to 35—55% of the total quantity present, whilst the diffusible calcium amounts to 30—40% of the total present. Milk freed from fat by centrifugal action contains 3% more ash-forming substances than does whole milk. W. P. S.

The Retention of Iron in the Organs in Hæmolytic Anæmia. ROBERT MUIR and JOHN SHAW DUNN (*J. Path. Bact.*, 1915, **19**, 417—428).—In acute hæmolytic anæmia nearly all the iron of the destroyed hæmoglobin is deposited in the liver, spleen, and kidneys; more than half the body hæmoglobin may be destroyed within three days. If hæmoglobinuria occurs, some iron escapes with the urine, and the amount of iron deposited in the kidneys is roughly proportional to this. A third of the iron of the blood may be deposited in the organs named within twenty-four hours. With regard to deposits of hæmosiderin, a broad distinction can be made between that resulting from lysis and that resulting from phagocytosis of red corpuscles. W. D. H.

The Neutralising Power of Saliva in its Relation to Dental Caries. JOHN ALBERT MARSHALL (*Amer. J. Physiol.*, 1915, **36**, 260—279).—A large number of human salivas were investigated with various indicators; the reaction found was very variable, whether caries was present or not, or whether the people took care to cleanse their teeth or not. As compared with resting saliva, "activated saliva" (that is, saliva collected after chewing) shows a smaller acidity and a rise in alkalinity. The magnitude of this factor is less in people free from caries than in those whose teeth are carious. W. D. H.

The Influence of Blood Transfusion on the Hyperglycæmia and Glycosuria of Pancreatic Diabetes in the Dog. A. J. CARLSON and H. GINSBURG (*Amer. J. Physiol.*, 1915, **36**, 280—293).—Transfusion of normal blood into dogs with pancreatic diabetes causes a lowering of the sugar in blood and urine which lasts four to eight hours. If diabetic blood is transfused, no effect follows. The effect is not due to kidney injury; there is indication that the temporary reduction of sugar excretion is followed later by an increase. W. D. H.

Fat in the Blood in a Case of Lipæmia. C. G. IMRIE (*J. Biol. Chem.*, 1915, **20**, 87—90).—In a fatal case of pancreatic disease, the blood-serum looked like cream; glycosuria was present. The serum contained: neutral fat and cholesterol, 14·06; cholesterol (unsaponifiable matter), 1·5; and fatty acids originally present in the form of soaps, 0·38%. Phosphatides were absent. The condition is explained on the supposition that mobilisation of connective tissue fat had occurred. W. D. H.

The Synthesis of Hippuric Acid in Experimental Tartrate Nephritis in the Rabbit. F. B. KINGSBURY and E. T. BELL (*J. Biol. Chem.*, 1915, **20**, 73—82).—Severe injury of the convoluted tubules does not affect the synthesis of hippuric acid. The glomeruli of collecting tubules are not seriously injured in tartrate nephritis. If the kidney really synthesises hippuric acid, which is doubtful in the rabbit, the synthesis must occur in glomeruli, the collecting tubes, or the degenerating cells of the convoluted tubules. W. D. H.

Affinity and Biological Activity of Acids. W. KOPACZEWSKI (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 420—432).—Acids act on various biological processes in different ways, and the order in which a series of acids can be arranged, corresponding with the magnitude of the action which they exert on one biological process, differs from the order for any other process. These statements are illustrated by various examples, and the conclusion reached is that the degree of dissociation and the hydrogen-ion concentration are not the only factors in determining the extent of action of the acids. H. W. B.

Colloidal State of Alkaloids. Relations between Surface Tension, Size of Particle, and Toxicity. I. TRAUBE and N. ONODERA (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 35—59).—Alkaloids such as atropine and quinine, the molecular weight of which exceeds a definite limit, are found, by means of the ultramicroscope, to be present in solution in a colloidal state, whilst the corresponding salts form true solutions. The surface tension of water is scarcely affected when salts of the alkaloids are dissolved in it, but when a small quantity of alkali is also added, the surface tension is diminished owing to the liberation of free alkaloid which forthwith assumes the colloidal condition. Corresponding with the diminished surface tension, there is increased toxicity of the solution, as has been ascertained experimentally with tadpoles, small fishes, etc.

Many of the free alkaloids are unstable in solution. In a few hours the small particles are seen under the ultramicroscope to become aggregated into large masses. In a corresponding degree the surface tension increases and the toxicity diminishes. On adding a little alkali to such an attenuated alkaloid solution, the aggregates disperse, the surface tension falls, and the toxicity reaches or surpasses its former intensity. It is suggested that the localisation of action of the various alkaloids may be partly due to the variation in the alkalinity of the different organs of the body. Where only a low degree of alkalinity exists, quinine, for example, might be potent and atropine inert, because quinine is found to be activated much more than atropine by alkali.

The toxicity of solutions of some of the alkaloids, as, for example, quinine, is increased by boiling and subsequently cooling them, and the authors have found that corresponding alterations occur in the size of the particle, surface tension, and toxicity. The antagonistic action of pilocarpine on atropine is accompanied by similar changes.

In a series of related alkaloids, the toxicity and surface tension increase as the molecular weight falls; and even when alkaloids of different classes are compared, it is found that the alteration in surface tension is the chief factor in determining the degree of toxicity. The hypothesis put forward to account for this relation between toxicity and surface tension is that any alteration in the surface tension disturbs the equilibrium or affects the normal velocity of the reactions taking place in the organism, and this becomes apparent as a toxic effect. The toxicity of alkaloids is due, apparently, chiefly to the physical instead of to the chemical changes produced.

The passage of an electric current through a solution of an alkaloid causes the smaller particles to wander towards the cathode, whilst the larger aggregates accumulate at the anode. H. W. B.

Synergism and Antagonism of Drugs and Poisons. I. TRAUBE and N. ONODERA (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 133—147. Compare preceding abstract).—The authors have studied the effect of the addition of one alkaloid to the solution of another on the

surface tension measured by the stalagmometer. The surface tension of quinine solutions is increased by atropine, aconitine, veratrine, and nicotine, and in relation to the latter drug it is suggested that smokers are probably more susceptible to quinine than non-smokers.

If an alkaloid is added to the solution of the salt of another alkaloid, the extent of alteration of the surface tension depends on the relative basicity of the two alkaloids. The relative toxicity of the alkaloids is given by the following series of basicities: nicotine>pilocarpine>atropine, physostigmine>quinine>aconitine>veratrine.

The effect on surface tension of combinations of solutions of various narcotics has been studied with results very similar to those recorded by Führer (A., 1914, i, 235). The action of nicotine is increased by ethyl carbamate, thymol, and chloral hydrate, and diminished by ether and chloroform. Alcohol and ether are antagonistic, whilst both ethyl carbamate and chloral hydrate are synergetic towards alcohol. The authors suggest that the latter substances may be more efficient narcotics than ether or chloroform for anæsthetising drunkards. The effect of narcotics on drugs affecting the heart's action was also investigated.

The authors point out that in the body the synergetic or antagonistic influence of two substances (drugs, narcotics, etc.) on each other may be due to an indirect action on the velocity of the protoplasmic reactions instead of to the direct action on the surface tension such as is considered in this communication. H. W. B.

Residual Valency of Anæsthetics and its Importance in Anæsthesia. Chemical Theory of Anæsthesia. A. P. Mathews (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 433—449).—The author points out that a direct relation is not apparent between the cohesional attractions of certain anæsthetics and their anæsthetising powers (compare A., 1914, ii, 643). The anæsthetic does not therefore become attached to protoplasm through the agency of this attraction. The author considers that the union between protoplasm and anæsthetic is due to the residual valency of the anæsthetic, and is of the nature of a molecular union. The average amount of residual valency per molecule possessed by various anæsthetics has been computed from the cohesion, and it is found that a general, but not complete, parallelism exists between anæsthetic power and amount of residual valency. Lack of complete parallelism may be due to the fact that the spatial relation of the valencies must also be important in determining anæsthetic power. The theory of anæsthesia put forward is that the irritable substance in protoplasm is a molecular oxygen–protoplasmic union, or a peroxide union, unstable and similar to oxyhæmoglobin. On stimulation this unstable molecular union passes by molecular rearrangement into a stable form, oxidation taking place and carbon dioxide being produced. The anæsthetic produces anæsthesia by occupying the oxygen receptors of the cell, thus forming a non-irritable, dissociable, anæsthetic–protoplasm compound. The

author explains the various phenomena of anæsthesia on this theory. H. W. B.

Narcosis. I. Effect of Ethyl Carbamate and Chloral Hydrate on the Carbon Dioxide Production of the Nerve Fibre. SHIBO TASHIRO and H. S. ADAMS (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 450—462).—The production of carbon dioxide by the claw nerve of the spider crab is greatly diminished after the nerve has been narcotised by placing in solutions of either ethyl carbamate or chloral hydrate of such concentrations as to produce a reversible loss of excitability. With a weak concentration of these narcotics, the carbon dioxide output is increased. This is in accord with the fact that these concentrations primarily stimulate or increase the irritability of the nerve. Certain nerves were found to be unexcitable without apparent cause, and the metabolism of such nerves, as measured by the carbon dioxide output, was invariably abnormally low.

The conclusion drawn by the authors is that metabolism in the nerve is interfered with by narcotics, and the results stand in agreement with Mathews' theory (preceding abstract), according to which the primary action of the narcotic on the protoplasm is to replace the oxygen, and thus interfere with the normal metabolism. H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Glycerol on Alcoholic Fermentation and on the Inversion of Sucrose. G. Rossi (*Boll. Chim. Farm.*, 1914, **53**, 657—659).—The fermentation of dextrose is not affected by the presence of 10·6 grams of glycerol per 100 c.c., but is retarded by 21·2, and inhibited by 42·3, grams per 100 c.c.; in the last case, the fermenting power of the yeast is permanently destroyed, subsequent dilution of the liquid not being followed by fermentation. The inversion of sucrose by yeast proceeds readily in presence of 50 grams of glycerol per 100 c.c. T. H. P.

The Enzymes of Aspergillus Terricola. F. M. Scales (*J. Biol. Chem.*, 1914, **19**, 459—472).—This mould produces inulase, diastase, invertase, maltase, alcohol-oxydase, emulsin, lipase, protease, tannase, and amidase; the fungus may therefore be concerned in the production of various organic decomposition products found in the soil. Many of these products are excellent sources of carbon and nitrogen for bacteria, and the ammonia produced may be directly assimilated as a salt by plants. The living organism hydrolyses a small amount of cellulose, but cellulase could not be isolated from the powdered material. Lactase and zymase are

absent. The fungus has no nitrogen-fixing power in nutrient solutions containing either carbohydrate or protein, or both.

W. D. H.

The Soluble Polysaccharides of Lower Fungi. III. The Influence of Autolysis on the Mycodextran Content of Aspergillus niger. ARTHUR W. DOX (*J. Biol. Chem.*, 1915, **20**, 83—85).—In various cultures of age varying from three to one hundred and forty-two days the yield % of mycodextran in the dried fungus increased from 0·9 to 9·2. This substance forms an integral part of the mature fungus, and does not undergo hydrolysis. The appearance of spores largely determines the larger yields. W. D. H.

Physiology of the Intake of Material by the Living Plant Cell. I. Lipo-colloids in the Plasma-membrane. FRIEDRICH CZAPEK (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 108—123).—A theoretical communication, partly polemical against Vernon (A., 1913, i, 802) and maintaining that the plasma membrane of animal cells differs from that of vegetable cells in containing lipo-colloids as well as hydro-colloids, the lipoids of the cell accumulating in the surface layers in accordance with the Gibbs-Thomson hypothesis. The capillarity law enunciated by the author as a result of his researches on vegetable cells cannot therefore be expected to hold strictly in the case of animal cells. H. W. B.

Physiology of the Intake of Material by the Living Plant Cell. II. Changes Produced by Potassium Cyanide in the Permeability of the Vegetable Plasma-membrane. MAX KREHAN (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 189—259).—After exposure of vegetable cells to dilute potassium cyanide solutions it is found that, as compared with similar cells preserved in water, considerably higher concentrations of certain substances in solution are required to bring about their plasmolysis. Of the substances tested, glycerol, lactose, dextrose, sucrose and most salts gave positive results; towards carbamide, sodium and potassium chlorides, and sodium nitrate the cells which had been treated with potassium cyanide behaved exactly like normal cells.

The effect of the potassium cyanide on the cells reaches a maximum when the cells have remained in the solution for a certain period of time which is the shorter the more concentrated the potassium cyanide solution. By longer contact the effect diminishes until after several hours the cells are found to be now more easily plasmolysed than normal cells. With low concentrations of potassium cyanide, the effect is a reversible one; and, after subsequent washing with water the cells become plasmolysed by the same concentration of the substance employed as before the treatment with the cyanide. With increasing concentration of potassium cyanide, however, the effect becomes irreversible.

The increased resistance to plasmolysis is shown by the author to be due to a specific action of the cyanogen ions. The same

effect on the cells is produced if the excess of hydroxyl ions in the cyanide solution is neutralised by the addition of an acid, and, moreover, dilute potassium hydroxide solution has only the slightest action on the cells. Ammonium hydroxide, on the contrary, behaves in a somewhat similar manner to potassium cyanide.

The condition of the vegetable cell is an important factor in determining the effect produced by potassium cyanide. During the winter the results obtained were only about a half of those obtained in summer, and neither differences of light intensity nor of temperature were found to be adequate to account for the variations observed.

Chloroform and the lower alcohols in low concentration increase the cyanide action, but in higher concentration the action is neutralised or even reversed.

The author regards the observed effects as being due to the direct action of potassium cyanide on the plasma colloids, and not to an inhibitory action of the cyanide on the respiratory activity of the cell. H. W. B.

Electric Charge of the Protoplasm and Other Substances in Living Cells. J. F. McClendon (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 159—162).—The anthocyan in the vacuoles of living cells of red cabbage is red, and on the passage of an electric current it moves towards the cathode (electrically positive). If alkali is added to the medium, the anthocyan becomes blue, and may now be observed to move towards the anode (electrically negative) before the death of the cell occurs. The anthocyan, therefore, seems to be an amphoteric substance like egg-albumin. It is suggested that protoplasm moves towards the anode because it is alkaline, but all attempts to acidify the protoplasm and obtain a movement towards the cathode were unsuccessful, owing to the death of the cell. H. W. B.

Effect of Acid on Permeability. W. J. V. Osterhout (*J. Biol. Chem.*, 1914, **19**, 493—501).—The method adopted was to determine the electrical resistance of the living tissues of *Laminaria saccharina*; this measures the permeability of the protoplasm; alkali increases permeability, acid decreases it rapidly; this is followed at once by a rapid increase, until the death-point is reached. W. D. H.

Antagonism Between Acids and Salts. W. J. V. Osterhout (*J. Biol. Chem.*, 1914, **19**, 517—520).—Further experiments on *Laminaria saccharina*. Acid antagonises the action of sodium chloride, but the degree of antagonism is not so great as between sodium chloride and calcium chloride. The favourable mixtures of these two salts maintain life longer than the most favourable mixtures of hydrochloric acid and sodium chloride. These results afford evidence that the plasma membrane in plants is protein in character. W. D. H.

Influence of the Chlorides and Nitrates of Potassium and Sodium on Germination. HENRI MICHEELS (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 412—419).—Wheat grains previously soaked in water have been germinated in dilute solutions ($M/100$ and $M/1000$) of potassium chloride and nitrate, sodium chloride and nitrate, and from the results the effects of the various ions have been deduced. The Cl-ion has a more injurious action than the NO_3-ion and the Na-ion than the K-ion. The NO_3-ion exerts a beneficial action especially in relation to the length of the leaves and the weight of the plantlet, and it also evokes a lengthening of the root-hairs. The Na-ion appears to lead to the formation of a longer root than is produced in the presence of K-ions.

The same results have been obtained by passing an electric current through the solutions and observing the germination of the grains in the neighbourhood of the cathode and anode respectively. H. W. B.

Influence of Fluorine on Vegetation. ARMAND GAUTIER (*Compt. rend.*, 1915, **160**, 194—195).—The author has compared the behaviour of various species of plants when grown in an artificial soil almost completely deprived of fluorine, in the same soil supplied with fluorine, and in ordinary arable soil. In a few cases fluorine appears to have an inhibitory effect, but in most cases it increases the growth, the flowering, and the production of seed. W. G.

Fruit of Clintonia Borealis. HORACE A. SLIPPY (*Chem. News*, 1915, **111**, 2—3).—The ripe berries, gathered at Sylvan Beach, New York, were indigo-blue in colour, had a very bitter taste, and each weighed about 0·34 gram; they lost about 75% of their weight when dried. The dry berries contained 4·87% of ash, 13·20% of total sugars, 8·75% of a gum-like substance, and small quantities of citric and tartaric acids. Prolonged extraction with ether yielded 4·22% of oil, but the extraction was not complete; this oil was of a deep green colour, owing to the presence of chlorophyll, but, after treatment with bone-charcoal, became light yellow. The oil was saponified with difficulty, and had $D^{15·5}$ 0·897. W. P. S.

Rate of Liberation of Hydrogen Cyanide from Commercial Varieties of Linseed. S. H. COLLINS and H. BLAIR (*Chem. News*, 1915, **111**, 19—20).—The authors have made observations with commercial varieties of linseed from different sources in order to ascertain the influence of the place of origin on the quantity of hydrogen cyanide, and the rate at which this is liberated. The results show that the seeds of Oriental origin are all rich in total hydrogen cyanide, and are also characterised by high enzymic activity. The seed from Morocco is low in respect of both these qualities.

The general effect of growing linseed in this country is to reduce the total amount of hydrogen cyanide, and to increase the activity of the enzyme.

From a comparison of the results obtained with linseeds grown under conditions of drought and high temperature with those grown under damp and low temperature conditions, it is found that the change from the former to the latter conditions is, on the average, accompanied by a fall of 20% in total amount of hydrogen cyanide, and by a reduction of 24% in the time required for the liberation of half the acid present. H. M. D.

The Red Thorn. Euclid C. Marston (*Chem. News*, 1914, **110**, 310).—This shrub belongs to the genus *Crataegus*, and is common from the North-Eastern United States to the Dakotas, and as far south as Missouri; it yields a dark red, woody fruit about 1 cm. in diameter. The dried fruit contains 35·37% of sugars, 0·76% of oil (probably laurin), 3·18% of ash, and 0·55% of nitrogen. Tartaric, citric, and acetic acids are present in the fruit, the last acid probably resulting from fermentation of the sugar.

W. P. S.

Iron in Tomatoes. C. A. Brautlecht and G. Crawford (*J. Ind. Eng. Chem.*, 1914, **6**, 1001—1002).—Tomatoes from ten counties in Florida were found to contain from 89·3 to 95·3% of water, 0·38 to 0·64% of ash, and 0·034 to 0·123% of ferric oxide. There was no fixed ratio between the water and ash or ferric oxide and ash; the ash contained from 4·38 to 22·25% of its weight of ferric oxide. The soils on which the tomatoes were grown contained from 3·03 to 3·72% of ferric oxide. W. P. S.

Toxicity of "Saccharin." E. Verschaffelt (*Pharm. Weekblad*, 1915, **52**, 37—46).—A comparison of the toxic action of "saccharin" on plants with that of other related substances. Both "saccharin" and its sodium derivative are less poisonous than sodium benzoate, but have more powerful toxic effects than related sulpho-compounds, such as sodium sulphobenzoate. It is suggested that "saccharin" may be a poison to all forms of protoplasm, and hence injurious to the human organism. A. J. W.

Determination of Certain Mineral Elements Necessary for the Development of Maize. P. Mazé (*Compt. rend.*, 1915, **160**, 211—214).—The author finds that maize plants will develop completely in an aseptic mineral solution prepared with spring water to which the eleven elements, nitrogen, phosphorus, potassium, calcium, magnesium, sulphur, iron, manganese, zinc, silicon, and cerium have been added, but that if distilled water is used instead of the spring water, the growth stops suddenly. The sudden stoppage of growth he considers is due to the absence of one or more elements from the culture medium. To the solution, therefore, one or more of the five elements, boron, aluminium, arsenic, iodine, and fluorine were added and cultures made. The results show that boron, aluminium, iodine, and fluorine are necessary for the development of maize, but that arsenic is injurious to this plant. These four elements probably complete the list of mineral elements necessary for the development of maize. W. G.

Chemical Investigation of the Phosphotungstate Precipitate from Rice Polishings. JACK CECIL DRUMMOND and CASIMIR FUNK (*Biochem. J.*, 1914, **8**, 598—615).—Choline and nicotinic acid are present in considerable amount; betaine, adenine, guanine, and possibly guanidine, are also present. Small quantities of other substances, not identified, also occur. The work of certain Japanese authors, who claim to have separated the curative material as a picrate, was not confirmed. It is apparently decomposed during fractionation, and all trace of it is lost. W. D. H.

Increased Nitrate Content of a Soil Subjected to Temporary Drying in the Laboratory. WALTER BUDDIN (*J. Agric. Sci.*, 1915, **6**, 452—455).—In soils which were spread out to dry, it was found that practically no change occurred either in bacterial numbers or in the amounts of nitrates present. When, however, the soils were kept for a month, there was a considerably greater increase in nitrates than in similar soils which had not been dried.

N. H. J. M.

Partial Sterilisation of Soils by Volatile and Non-volatile Antiseptics. WALTER BUDDIN (*J. Agric. Sci.*, 1915, **6**, 417—451. Compare Russell and Buddin, A., 1914, i, 242).—When antiseptics are applied to soils in amounts sufficient to bring about the usual partial sterilisation effects, no increase causes any further change.

The paraffin hydrocarbons have so little effect that they can hardly be considered as antiseptics. Their employment results, however, in a depression in bacterial numbers and in a decided increase in the amount of ammonia; the nitrifying organisms and the Protozoa are not suppressed. Results similar to these, although less marked, are obtained by merely air-drying the soils, in thin layers, for twenty-four hours. Non-volatile antiseptics give rise to a permanent depression in bacterial numbers with the highest amounts. The stronger ones, such as quinone and quinol, show an initial depression in bacterial numbers when only about 0·05% is used, whilst weaker antiseptics, applied at the same rate, merely liberate small amounts of ammonia.

The traces of substances left in the soil when non-volatile antiseptics are used, generally produce, at varying periods, a great rise in the number of some special organisms. The new bacterial flora does not produce ammonia; and none of the non-volatile antiseptics give rise to so great a production of ammonia and nitrates as results from the application of volatile antiseptics. N. H. J. M.

Organic Chemistry.

Action of Acetylene on Metals. H. Reckleben and Joh. Scheiber (*Chem. Zeit.*, 1915, **39**, 42).—Three series of metals and alloys were exposed for twenty months to the action of a slow stream of acetylene; in the one case the gas was crude and moist, in the second purified by passing through copper, iron, and lead solutions, and in the third series it was also dried in addition. The pure dry gas was found to have no action on any of the metals examined, they remained unaltered in appearance and weight. Pure moist acetylene caused with nickel 0·9% and with copper 1·6% increase in weight; in other cases no action occurred. Crude moist acetylene left tin, German silver, aluminium bronze, type metal, and solder almost unattacked. With zinc, lead, brass, and nickel increases in weight of 0·4—0·9% were observed, with iron 6·4%, and with phosphor bronze 14·4%, the latter two having lost their metallic appearance. Copper was attacked very rapidly, showing an increase in weight of 80—90% in six months, and being converted into a black, non-explosive substance which did not give acetylene on treatment with acids, and left a black insoluble carbon compound of a humic nature. It is evident from the experiments that copper should not be used for acetylene gas tubing, and in fact the tinning of any metal or alloy with which acetylene comes in contact is obviously advantageous. G. F. M.

Catalytic Actions of Colloidal Metals of the Platinum Group. XII. Progressive Reduction of Acetylene. C. Paal and Christian Hohenegger (*Ber.*, 1915, **48**, 275—287).—The catalytic reduction of acetylene to ethylene has often been attempted, but many workers, including Sabatier and Senderens, have found that even if insufficient hydrogen to complete the first stage is employed, the chief product is ethane. Acetylenic derivatives, however, have been successfully reduced in stages by catalytic methods, for example, phenylpropiolic acid (A., 1909, i, 926) and phenylacetylene and diphenyldiacetylene (A., 1912, i, 617). Moreover, since the present work was completed (Hohenegger, *Diss.*, Erlangen, 1912) Karo has patented a method for the preparation of ethylene from acetylene in which the catalysts employed are platinum metals diluted with baser metals (D.R.-P. 253160).

The present investigation has been conducted with colloidal palladium. The numerous experiments, partly in a gas burette, partly in a vessel which could be shaken and partly in an apparatus in which the gases could be circulated, are described in detail. The chief result is the demonstration of the influence of the adsorption of acetylene by palladium on the course of the reaction. Starting with equal volumes of acetylene and hydrogen, and with a fresh palladium solution, so much of the former gas is adsorbed by the colloid and chemically changed, in all probability polymerised (A.,

1913, i, 241) that the hydrogen is really in effective excess, with the result that varying volumes of ethane are formed and some acetylene remains unchanged. When the colloid has been in contact with acetylene, it loses the power of adsorbing the gas and the yield of ethylene increases. Indeed, with a slight excess of acetylene, all the hydrogen may be used in the formation of ethylene.

The mixtures of gases were analysed as follows. The two unsaturated hydrocarbons were absorbed by bromine water and the acetylene estimated separately by an approximate method (described in the original dissertation) in which an ammoniacal silver solution was used as the absorbent. Hydrogen was estimated in the residue by absorption with palladium hydrosol and sodium picrate (A., 1910, ii, 237) and the ethane (and impurities) measured by difference. J. C. W.

Production of Chloropicrin by the Action of Aqua Regia on Organic Compounds. RASIK LAL DATTA and NIHAR RANJAN CHATTERJEE (*J. Amer. Chem. Soc.*, 1915, **37**, 567—569).—Datta and Fernandes (A., 1914, i, 675) and Datta (A., 1914, i, 701) have shown that aqua regia reacts as a chlorinating agent as well as an oxidising agent. It has now been found that, in some cases, it decomposes organic substances with formation of chloropicrin.

When acetone is added gradually to a mixture of nitric acid (two parts) and hydrochloric acid (three parts) and gently warmed, a nearly quantitative yield of chloropicrin is obtained. This is recommended as the best method for preparing chloropicrin. If the reaction is carried out without the aid of heat, chloropicrin is produced together with a colourless, crystalline substance, m. p. 103—104°.

Allyl alcohol can be converted quantitatively into chloropicrin by the same method. Ether yields a small quantity of chloropicrin. Ethyl alcohol is partially decomposed with formation of chloropicrin, but methyl alcohol and formic and acetic acids resist the action of aqua regia even when warmed with it. E. G.

Action of Metals on the Chlorides of Carbon. ENRIQUE V. ZAPPI (*An. Soc. Quím. Argentina*, 1914, **2**, 217—228).—A study of the interaction at ordinary and elevated temperatures of aluminium, magnesium, iron, sodium, and silicon respectively and carbon tetrachloride, hexachloroethane, hexachlorobenzene, and octachloronaphthalene. At 180°, aluminium decomposes carbon tetrachloride, liberating carbon, and forming hexachloroethane and aluminium chloride. Under other conditions aluminium has no action on any of the substances named, or only a very slight effect. The other metals either do not react at all, or only to a very limited degree. A. J. W.

The Decomposition of Heptachloropropane, $CCl_3 \cdot CCl_2 \cdot CHCl_2$, by Heat and by Means of Some Catalysts. J. BÖESEKEN, J. VAN DER SCHEER, and J. G. DE VOOGT (*Rec. trav. chim.*, 1915, **34**, 78—95; compare A., 1911, i, 173).—Heptachloropropane is decomposed by heat into hexachloropropylene and hydrogen chloride, the decomposition being slightly accelerated by zinc chloride, but hardly

at all by barium chloride. With cuprous chloride as a catalyst, the decomposition takes place in two ways, one yielding hexachloropropylene and hydrogen chloride, the other yielding tetrachloroethylene and chloroform, the latter being the more pronounced at temperatures above 250°. With aluminium chloride as catalyst, the results show that the equilibrium $C_3HCl_7 \rightleftarrows C_2Cl_4 + CHCl_3$ is at 110° displaced considerably towards the right, whilst at this temperature the decomposition $C_3HCl_7 = C_3Cl_6 + HCl$ is not reversible. At 65° the first method of decomposition is more active than the second, the equilibrium being more towards the right. Complete equilibrium of

$$C_3HCl_7 \rightleftarrows C_2Cl_4 + CHCl_3$$

cannot be attained owing to the secondary decomposition into hexachloropropylene and hydrogen chloride. W. G.

Acetylenic Compounds. R. Lespieau (*Ann. Chim.*, 1914, [ix], **2**, 280—292).—A more detailed account of work already published (compare A., 1914, i, 134, 476, 650). W. G.

Preparation of Optically Active Dibromopropionic Acid Configuration of Optically Active Glycerol Derivatives. Their Relation to Glyceric Acid. Emil Abderhalden and Egon Eichwald (*Ber.*, 1915, **48**, 113–117. Compare A., 1914, i, 801).—In continuation of the work on the synthesis of optically active fats, the authors have prepared active $\alpha\beta$-dibromopropionic acid and have determined the configuration of the halogenhydrins by oxidation of *d*-epibromohydrin to *l*-bromolactic acid. Since the connexion between the latter and *l*-glyceric acid has been established by Freudenberg (A., 1914, i, 925) the following scheme may be given:

d-Dibromohydrin → *d*-epibromohydrin → *l*-bromolactic acid

↓ ↓

d-dibromopropionic acid *l*-glyceric acid.

Since further, potassium *l*-glycidate is obtained from *d*-bromolactic acid into which it is reconverted by the action of hydrobromic acid, the authors consider that the possibility of an inversion during the formation or opening of the glycide-ring is excluded.

The active *αβ-dibromopropionic acids* are obtained from the active dibromohydrins by oxidation with nitric acid (D 1·4) in the manner recommended for the corresponding inactive compounds. Since, however, the active acids appear to be more susceptible to oxidising agents than the inactive acid, the period of action must be curtailed. The acid is purified by freezing and by treatment with water. The *d*-acid melts at a considerably lower temperature than the inactive isomeride; it has $[\alpha]_D^{18} + 13{\cdot}76°$ in water, $[\alpha]_D^{18} + 6{\cdot}42°$ in alcohol. The specimens of *l*-acid obtained had $[\alpha]_D^{18} - 2{\cdot}44°$ in water. *Ethyl* d-*αβ-dibromopropionate* has $[\alpha]_D^{18} + 9{\cdot}77°$ in alcohol.

Oxidation of a specimen of *d*-epibromohydrin, $[\alpha]_D + 15{\cdot}48°$, by 38% nitric acid gave *l*-bromolactic acid, $[\alpha]_D - 2{\cdot}91°$ in alcohol. Comparison of this acid with the pure acid obtained by Freudenberg's method (*loc. cit.*) shows it to contain about 40% of the racemic acid.

The optically active *potassium glycidates*, $\begin{matrix}O\text{—}\\ |\\ CH_2\end{matrix}\!>\!CH\cdot CO_2K$, have been obtained from the corresponding bromolactic acids by Freudenberg's method, careful cooling, however, being necessary in order to avoid racemisation. *d*-Bromolactic acid thus yielded potassium *l*-glycidate, $[\alpha]_D^{18} - 11{\cdot}70°$ in water, whereas the *l*-isomeride gave potassium *d*-glycidate, $[\alpha]_D^{18} + 30{\cdot}16°$. From potassium *l*-glycidate a dextrorotatory bromolactic acid was obtained. H. W.

Action of Finely Divided Silver on α-Bromo- and α-Iodo-palmitic Acids: Synthesis of Two Isomeric Di-tetradecylsuccinic Acids. D. Breese Jones (*J. Amer. Chem. Soc.*, 1915, **37**, 586—594).—It has been shown by Hell and his co-workers that when halogen derivatives of the aliphatic acids are treated with finely divided silver, the reaction products in nearly all cases contain two isomeric dialkylsuccinic acids. A study has now been made of the action of silver on α-bromo- and α-iodo-palmitic acids.

When α-bromo- or α-iodo-palmitic acid, dissolved in heptane, is boiled with finely divided silver for nine hours, a product is obtained containing palmitic acid, two isomeric *s*-di-tetradecylsuccinic acids, and an unsaturated acid which was not identified.

The two forms of *s-di-tetradecylsuccinic acid*,

$$\begin{matrix}CH_2Me\cdot[CH_2]_{12}\cdot CH\cdot CO_2H\\ CH_2Me\cdot[CH_2]_{12}\cdot CH\cdot CO_2H'\end{matrix}$$

melt at 135—136° and 95—96° respectively. The higher melting form is very slightly soluble in most organic solvents whilst the other is fairly soluble. When the acid of m. p. 135° is heated at about 170°, it is converted into the *anhydride*, $\begin{matrix}CH_2Me\cdot[CH_2]_{12}\cdot CH\cdot CO\\ CH_2Me\cdot[CH_2]_{12}\cdot CH\cdot CO\end{matrix}\!>\!O$, m. p. 45—45·5°, which on hydrolysis furnishes the acid of m. p. 95°. The latter acid loses water at 150° and is converted into an unstable *anhydride* which readily undergoes transformation into the anhydride of m. p. 45°. The acid, melting at 135°, was obtained in a yield of 8% of the calculated from α-bromopalmitic acid, and in a yield of 13% from α-iodopalmitic acid. The yield of the acid melting at 95° is considerably less. It is considered probable that the higher melting acid is the *meso*-form, and the lower melting acid the racemic form.

E. G.

Syntheses by Means of Mixed Organometallic Derivatives of Zinc. γ-Chloroketones and Transformation Products. Henri Wohlgemuth (*Ann. chim.*, 1914, [ix], **2**, 292—332).—For the most part a résumé of work already published (compare A., 1914, i, 800, 929). In the latter part of the paper a proof is given of the constitution of a neutral secondary product, obtained in the action of diethylamine on γ-bromovaleric acid. This substance is now shown to be *ethyl allylacetate* [*Δ$^{\gamma}$-pentenoate*], $CH_2{:}CH\cdot CH_2\cdot CH_2\cdot CO_2Et$, b. p. 39—40°/8 mm. It is insoluble in water and instantly decolorises potassium permanganate solution. It is best obtained by boiling ethyl γ-chlorovalerate (21·5 grams) for one hour with quinoline (45 grams.). On

hydrolysis with aqueous alcoholic potassium hydroxide it yielded Δ^{γ}-*pentenoic acid*, $C_5H_8O_2$, b. p. 89—91°/12·5 mm., giving an *acid chloride*, b. p. 62—64°/72—73 mm. and an *anilide*, m. p. 92°. In the preparation of the anilide a small amount of an isomeric *anilide*, m. p. 45°, was obtained, but not characterised. On oxidation Δ^{γ}-pentenoic acid gave succinic acid and carbon dioxide.

In proving the constitution of the above compounds Δ^{γ}-pentenoic acid has been prepared from allylmalonic acid, and in addition the author has prepared two of its isomerides. Δ^{β}-*Pentenoic acid*,

$$CH_3{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CO_2H,$$

b. p. 94—96°/16 mm. obtained by heating methylparaconic acid. The acid gives an *ethyl* ester, b. p. 51—52°/15·5 mm., a *methyl* ester, b. p. 42—43°/18 mm. and 72—75°/87 mm., and an *anilide*, m. p. 72°. Δ^{α}-Pentenoic acid (compare Crossley and Le Sueur, T., 1899, **75**, 166) gives an *anilide*, m. p. 98—99°. W. G.

The Composition of Paint Vapours. C. A. Klein (*J. Ind. Eng. Chem.*, 1915, **7**, 99–102).—A criticism of a recent paper by Gardner (A., 1914, i, 380).—The author maintains that no evidence has been brought forward to justify the assertion that carbon monoxide is present or can be detected in paint vapours; the carbon monoxide detected and estimated by Gardner may have been derived from the action of the fuming sulphuric acid on the formic acid and other organic compounds in the paint vapours. The author discusses the question of the changes in weight observed during the drying of linseed oil and linseed oil paints and points out the many factors which influence the problem. W. P. S.

Selenoaldehydes. L. Vanino and A. Schinner (*J. pr. Chem.*, 1915, [ii], **91**, 116–127).—The selenium analogues of formaldehyde, acetaldehyde, and benzaldehyde have been prepared by the action of hydrogen selenide on the corresponding aldehydes.

Selenoformaldehyde, $CH_2{:}Se$, obtained by passing hydrogen selenide into 36% aqueous formaldehyde mixed with three times its volume of concentrated hydrochloric acid, separates from alcohol in columnar crystals, m. p. about 215°. It is very sparingly soluble in most organic media and becomes light green on exposure to sunlight.

When hydrogen selenide is passed into a solution of acetaldehyde in three times its volume of alcohol, saturated with hydrogen chloride, and the resulting semi-solid mass crystallised from alcohol, a *seleno-acetaldehyde*, $CH_3{\cdot}CHSe$, is obtained in slender, transparent needles, m. p. 139°; the residue, left on evaporating the alcoholic solution separates from acetone in crystals of m. p. 123–124°. If chloroform is used as a solvent, the resulting product has m. p. 117°. Selenoaldehyde thus resembles thioacetaldehyde in existing in several modifications.

α-Selenobenzaldehyde, prepared by passing hydrogen selenide for 3—4 hours into an alcoholic solution of benzaldehyde, crystallises in clusters of yellow, transparent columns, m. p. 83—84°; if the alcohol is previously saturated with hydrogen chloride, a mixture of β-and γ-selenobenzaldehydes is obtained, which may be separated by taking advantage of their different solubilities in benzene. *β-Selenobenzalde-*

hyde is the more sparingly soluble form, and crystallises from benzene in lustrous, golden-yellow needles of the composition $3C_6H_5\cdot CHSe,C_6H_6$, m. p. about 205°.

The benzene mother-liquors yield on evaporation *γ-selenobenzaldehyde*, which crystallises in slender, pale yellow needles, m. p. 166°.

When distilled with copper powder β-selenobenzaldehyde is converted into stilbene.

Hydrogen selenide is readily prepared by the action of water on aluminium selenide. F. B.

Molecular Weight of Acetone in Freezing Carbon Tetrachloride and in Chloroform. E. Beckmann and O. Faust. (*Zeitsch. physikal. Chem.*, 1914, **89**, 247–251).—The molecular weight of acetone in carbon tetrachloride was determined for concentrations up to 3%. Extrapolation of the results shows that in infinitely dilute solution acetone exhibits a normal molecular weight, but with increasing concentration the molecular weight increases, showing that considerable association has taken place, a fact which is also shown in vapour pressure determinations. The freezing point constant of chloroform has been redetermined, using toluene and ethyl ether and measuring the temperatures with a resistance thermometer capable of reading to 0·001°. A value of 49·0 was obtained in both cases. On attempting to determine the molecular weight of acetone in chloroform solution results were obtained which indicate that at the temperature of −65° acetone and chloroform unite to form a chemical compound just as they do at higher temperatures. This was confirmed by dropping acetone on frozen chloroform, when considerable rise of temperature occurred. J. F. S.

Halogenation. VIII. New Series of Chlorohydroxy-compounds. Hydrolytic Chlorination of Dimethylpyrone. Isolation of βγεζ-Tetrachloro-βζ-dihydroxyheptan-δ-one and its Decomposition into γε-Dichloroheptan-βδζ-trione. Rasik Lal Datta and Satyaranjan Das Gupta (*J. Amer. Chem. Soc.*, 1915, **37**, 578—582).—When dimethylpyrone is treated with chlorine, or with potassium chlorate and hydrochloric acid, or with aqua regia, it is converted into *βγεζ-tetrachloro-βζ-dihydroxyheptan-δ-one*,

$$CO(CHCl\cdot CMeCl\cdot OH)_2,$$

which is obtained as a pale yellow, somewhat viscous oil. This substance gradually decomposes with evolution of hydrogen chloride and production of *γε-dichloroheptan-βδζ-trione*, $CO(CHCl\cdot COMe)_2$, m. p. 145—146°, which forms colourless crystals. E. G.

Partial Acylation of Polyhydric Alcohols and Sugars. Emil Fischer (*Ber.*, 1915, **48**, 266—275).—The acetone compounds of dulcitol and mannitol, that is, derivatives in which some of the hydroxyl groups are rendered dormant, have been benzoylated in the presence of quinoline and then deprived of the acetone residues by the action of glacial acetic acid containing a little hydrogen chloride. Partially benzoylated alcohols have thus been prepared in the pure state.

The dulcitoldiacetone, m. p. 98°, prepared in 1895 (Speier, A., 1896, i, 77) was a mixture of two isomerides. These may be separated by fractional crystallisation from an acetone-light petroleum solution into *dulcitol-α-diacetone*, stout, many-sided crystals, m. p. 145—146°, and *dulcitol-β-diacetone*, well-developed sheaves of needles or prisms, m. p. 113—114° (corr.). The former modification is obtained in larger yield by shaking the dulcitol with a slightly stronger acetone solution of hydrogen chloride than was originally adopted and, after removing the acid by means of silver carbonate, evaporating the product under the ordinary pressure. On the other hand, the β-form predominates if a weaker acid is used and the solution is worked up earlier.

Dibenzoyldulcitol-α-diacetone, $C_6H_8O_6Bz_2(C_3H_6)_2$, is prepared by heating a mixture of the α-diacetone with quinoline (2·2 mol.) and benzoyl chloride (2 mol.) on the steam bath for 5—6 hours. The mass of crystals, which begins to separate early, is ground with alcohol, which removes quinoline hydrochloride and impurities, and then crystallised from carbon tetrachloride. The substance forms well-developed, four-sided prisms, m. p. 185—186° (corr.). If pyridine is employed instead of quinoline, another *compound* of the same composition is formed, in needles, m. p. 82—83°. *Dibenzoyldulcitol*, $C_6H_{12}O_6Bz_2$, is prepared by shaking the above derivative with a 5% solution of hydrogen chloride in glacial acetic acid. It forms four-sided platelets, m. p. 210° (corr.) and may be distilled without decomposition. If the benzoylation of dulcitol-α-diacetone be carried out at the ordinary temperature, a mono-benzoyl derivative is formed, as an oil. This is hydrolysed by shaking with chloroform and 5*N*-hydrochloric acid to *monobenzoyldulcitol*, $C_6H_{13}O_6Bz$, which forms thin needles, m. p. 155—156° (corr.).

Mannitolmonoacetone (Irvine and Paterson, T., 1914, **105**, 907, 908) was also left with quinoline (4·5 mol.), benzoyl chloride (4·5 mol.) and chloroform for five days, when the solution was washed with water and evaporated. *Tetrabenzoylmannitolmonoacetone*, $C_6H_8O_6Bz_4{\cdot}C_3H_6$, was thus formed, in slender plates, m. p. 122—123° (corr.), $[\alpha]_D^{20}$ +0·60° in *s*-tetrachloroethane and +15·42° in toluene. This was hydrolysed as above to *tetrabenzoylmannitol*, $C_6H_{10}O_6Bz_4$, which is microcrystalline and has m. p. 122—123° (corr.), and $[\alpha]_D^{18}$ +7·83° in *s*-tetrachloroethane.

The author dissociates himself from the definite views concerning the structure of the acetone compounds, which Irvine and Paterson ascribed to him (*ibid.*, p. 900) and leaves the question open.

J. C. W.

Gentiobiose. Géza Zemplén (*Ber.*, 1915, **48**, 233—238).—The biochemical synthesis of gentiobiose by the action of emulsin on dextrose, which was achieved by Bourquelot, Hérissey and Coirre (A., 1913, i, 1305) does not accord with E. F. Armstrong's statement (*The Simple Carbohydrates and the Glucosides*, 1912, p. 97) that maltose may be obtained in this way.

The formation of an α-disaccharide, like maltose, is also contrary to the established rule that enzymes only bring about the synthesis of those disaccharides which, under other conditions, are hydrolysed in

their presence. In the case of emulsin these would be β-disaccharides like gentiobiose, cellobiose, or *iso*maltose.

The author has therefore repeated Bourquelot's work with positive results, for he has isolated the octa-acetate and phenylosazone of gentiobiose from the product of the action of emulsin on a 50% dextrose solution.

With the idea of deciding whether gentiobiose is identical with *iso*maltose or not, syrups containing the latter have been prepared by Fischer's method (A., 1891, i, 412) and acetylated. Although the octa-acetate of gentiobiose is readily isolated from very impure products (A., 1913, i, 707), it could not be obtained from these syrups and it seems to be highly probable, therefore, that gentiobiose and *iso*maltose are not identical. J. C. W.

Chloro-salts of Ruthenium [Ruthenichlorides]. A. GUTBIER and FERDINAND KRAUSS (*J. pr. Chem.*, 1915, [ii], **91**, 103—115; compare A., 1911, i, 183; 1907, i, 289).—An account of the preparation and properties of a number of substituted ammonium ruthenichlorides derived from the following three types:—

I. $(NH_4)_2RuCl_6$, II. $(NH_4)_2RuCl_5$, and III. $(NH_4)_4RuCl_7$

[With F. KRAUSS.] The following pentachloro-compounds (II) were prepared by mixing concentrated solutions of the substituted ammonium chlorides and ruthenic chloride in dilute hydrochloric acid. With the exceptions indicated below, they all separate in lustrous, black crystals. *Methylammonium ruthenipentachloride*, $(NH_3Me)_2RuCl_5$, lustrous reddish-black crystals; *dimethylammonium* $(NH_2Me_2)_2RuCl_5$; *trimethylammonium*; *tetramethylammonium*; *ethylammonium*; *diethylammonium*; *triethylammonium*; *tetraethylammonium*; *propylammonium*, needles; iso-*propylammonium*, needles; *dipropylammonium*, lustrous, red crystals; *tripropylammonium*, reddish-black needles having a vivid lustre; *butylammonium*; iso*butylammonium* lustrous, reddish-brown crystals; *di*-iso-*butylammonium*, lustrous, dark red crystals; *tri*-iso-*butylammonium*; *guanidinium*, $[NH:C(NH_2)_2]_2RuCl_5$, lustrous, dark red crystals; *ethylenediammonium*, $C_2H_4(NH_3)_2RuCl_5$, small, red crystals; *pyridinium*, hygroscopic, golden-yellow crystals; *β-picolinium* $(C_5H_4Me_5{\cdot}N)_2RuCl_5$; *piperidinium*, black needles; *quinolinium*, lustrous, dark red crystals.

The following new hexachloro-compounds (type I) were prepared by the methods already described (A. 1907, i, 289): *tetramethylammonium* $(NMe_4)_2RuCl_6$; *tetraethylammonium*; *tripropylammonium*; *di*-iso-*butylammonium*; *tri*-iso*butylammonium*; *di*-iso*amylammonium*, lustrous, red crystals; *guanidinium*, $[NH:C(NH_3)_2]_2RuCl_6$; *β-picolinium*; *piperidinium*; *quinolinium*. With the exception of the di-*iso*amylammonium salt, all the above compounds form lustrous, black crystals.

[With HERMANN ZWICKER.]—In attempts to prepare the corresponding pentachloro-derivatives by the method described above, the following compounds of the heptachloro-series (type III) were obtained: *methylammonium*, $(NH_3Me)_4RuCl_7$, lustrous, dark reddish-brown needles; *ethylammonium*, lustrous, reddish-brown, feathery needles or small, irregular plates; *ethylenediammonium*, $[C_2H_4(NH_3)_2]_2RuCl_7$, red

to brownish-red, small, lustrous, needles or leaflets; *propylenediammonium*, glistening, purple-red leaflets and needles. F. B.

Preparation of Hexamethylenetetramine Di-iodide. M. Rix (D.R.-P., 278,885; from *J. Soc. Chem. Ind.*, 1915, **34**, 250; compare this vol., i, 6).—Powdered hexamethylenetetramine and iodine react speedily in the presence of traces of inert solvents, as, for example, alcohol, in quantity insufficient to make the mixture sensibly moist. J. C. W.

Synthesis of Polypeptides by the Action of Glycerol on Glycine; Dynamic Study. L. C. Maillard (*Ann. Chim.*, 1914, [ix], **2**, 210—268).—A study of the conditions governing the actions between glycerol and glycine already recorded qualitatively (compare A., 1912, i, 13; 1914, i, 940). The author has first studied the effect of duration of heating, the temperature of heating the mixtures being raised during two hours to 175° and then maintained at that level for ten-and-a-half hours, test portions of the mixture being withdrawn every half hour. After the first two hours at 175°, the glycine begins to condense, yielding anhydrides without any other change or loss. The condensation takes place in two ways, one yielding *cyclo*glycylglycine, the other an open chain tetrapeptide, triglycylglycine, the amount of this compound steadily increasing with the time. At the end of five hours a brown colour begins to develop in the reaction mixture, a nitrogenous derivative of glycine other than an anhydride being formed. After a time nitrogen is lost from the mixture owing to volatilisation of the *cyclo*glycylglycine, and the triglycylglycine yields a *cyclo*polyglycylglycine.

The author also tried the effect of varying the proportion of glycerol to glycine and found that 4 parts of glycerol (D 1·26) to 1 part of glycine gave the best yield of *cyclo*glycylglycine. Diminishing the amount of glycerol gave rise to the formation of *cyclo*polyglycylglycine through the intermediary of triglycylglycine.

The course of the reaction as explained by the author is that unstable glyceryl glycinate is first formed and this then breaks down, giving *cyclo*glycylglycine and glycerol. Representing glycerol by the formula R·OH, the formation of *cyclo*glycylglycine is shown by the equations

$$NH_2\cdot CH_2\cdot CO_2H + R\cdot OH = H_2O + NH_2\cdot CH_2\cdot CO_2R,$$

$$2NH_2\cdot CH_2\cdot CO_2R = \begin{matrix} NH\cdot CH_2\cdot CO \\ | \quad\quad | \\ CO\cdot CH_2\cdot NH \end{matrix} + 2R\cdot OH$$

and of triglycylglycine by

$$NH_2\cdot CH_2\cdot CO_2H + R\cdot OH = H_2O + NH_2\cdot CH_2\cdot CO_2R$$

$$2NH_2\cdot CH_2\cdot CO_2R = R\cdot OH + NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2R$$

$$2NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2R =$$

$$R\cdot OH + NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2R,$$

the last compound then undergoing hydrolysis, the formation of the more complex compounds being represented in a similar manner.

The author considers that it is by reactions of this character that proteins are built up from simple amino-acids in the body. W. G.

Halogenation. VII. Substituted Nitrogen Chlorides. Action of Chlorine on Carbamic Esters and Biurets and the Preparation of Chlorocarbamic Esters and Chlorobiurets. RASIK LAL DATTA and SATYARANJAN DAS GUPTA (*J. Amer. Chem. Soc.*, 1915, **37**, 569—578).—In an earlier paper (A., 1914, i, 257), it has been shown that ethyl chlorocarbamate can be prepared by the action of chlorine on a well cooled, aqueous solution of ethyl carbamate. The reaction has now been extended to the chlorination of other carbamates and also of biuret and its derivatives. The alkyl chlorocarbamates are generally pale yellow liquids, and are soluble in most of the usual organic solvents. When applied to the skin, they produce painful blisters.

In the case of methyl carbamate, a chloro-derivative cannot be obtained. Propyl carbamate yields either a mono- or di-chloro-derivative according to the amount of chlorine passed into the solution. *Propyl chlorocarbamate*, $NHCl{\cdot}CO_2Pr^{\alpha}$, has D^{30} 1·269 and n_D^{30} 1·45377. *Propyl dichlorocarbamate* forms a pale yellow, mobile liquid, but could not be obtained in a pure condition. *iso*Butyl carbamate also furnishes mono- and di-chloro-derivatives. iso*Butyl chlorocarbamate*, $NHCl{\cdot}CO_2{\cdot}C_4H_9$, has D^{30} 1·156 and n_D^{30} 1·44615, and when heated at 140°, it begins to boil and suffers decomposition, leaving a white solid. The *dichloro*-derivative could not be obtained in a pure state. In the case of *iso*amyl carbamate, the dichloro-derivative is produced but the monochloro-derivative cannot be obtained. iso*Amyl dichlorocarbamate*, $NCl_2{\cdot}CO_2{\cdot}C_5H_{11}$, has D^{30} 1·156 and n_D^{30} 1·45146; it begins to boil at 124° and undergoes violent decomposition at 145°.

When diethyl ethylidenecarbamate (ethylideneurethane),

$$CH_3{\cdot}CH(NH{\cdot}CO_2Et)_2,$$

is treated with chlorine, it is converted into *ethyl dichlorocarbamate*, $NCl_2{\cdot}CO_2Et$, which has D^{30} 1·304 and n_D^{30} 1·45397. Chloralurethane is not attacked by chlorine. When phenyl carbamate, suspended in water, is treated with chlorine, a condensation *product*, $C_{18}H_{20}O_9N_3Cl_2$, m. p. 83°, is produced, which forms white needles.

When ethyl chlorocarbamate is left for several days in contact with aqueous alkali in presence of air, it is decomposed with formation of a crystalline *compound*, $C_7H_{15}O_4N_3Cl$, m. p. 147°.

By the action of chlorine on an aqueous solution of biuret, *dichlorobiuret*, $NH(CO{\cdot}NHCl)_2$, m. p. 160° (decomp.), is produced as a crystalline powder which is quite stable. Acetylbiuret is similarly converted into *acetyldichlorobiuret*, $NHAc{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NCl_2$, m. p. 170° (decomp.). In the case of benzoylbiuret, a chloro-derivative could not be obtained. E. G.

Preparation of Acylated Isocarbamide Ethers. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P., 277,466.)—When the *iso*carbamide ethers or their salts are treated with α-bromo*iso*valeryl haloids, they are converted into the α-bromo*iso*valeryl*iso*carbamide ethers, which are feebly basic, and act promptly and without ill effects as sedatives.

*α-Bromoisovaleryl*isocarbamide *methyl ether*,

$$CHMe_2{\cdot}CHBr{\cdot}CO{\cdot}NH{\cdot}C(OMe){:}NH,$$

is prepared by adding the acid bromide to methyl*iso*carbamide (A., 1900, i, 431) in cold, ethereal solution, and evaporating the filtrate. It is an oil which may be distilled in small quantities, b.p. 149°/5 mm. *α-Bromoisovalerylisocarbamide ethyl ether* is prepared, as an alternative, from the hydrochloride of ethyl*iso*carbamide (*ibid.*). A mixture of this salt with *α*-bromo*iso*valeryl bromide and benzene is gradually treated with 30% potassium hydroxide in the cold. Both oils are converted into *α*-bromo*iso*valerylcarbamide, with elimination of the alkyl chloride, when warmed with hydrochloric acid.

J. C. W.

The Action of Oxalyl Chloride on Some Derivatives of Hydrazine. T. FOLPMERS (*Rec. trav. chim.*, 1915, **34**, 34—77).—The first part of the paper is a résumé of work already published on the subject. The author has examined the condensation products of oxalyl chloride with three different types of hydrazine derivatives. In the case of those containing only one substituent, namely, methyl-, phenyl-, acetyl-, and benzoyl-hydrazines, the unsubstituted $\cdot NH_2$ group of the hydrazine reacted with the oxalyl chloride, giving substances of the type oxalyl-bis-*β*-methylhydrazide, NHMe·NH·CO·CO·NH·NHMe. Only in the case of methylhydrazide were other condensation products obtained, *oxalyl-bis-α-methylhydrazide*, $NH_2 \cdot NMe \cdot CO \cdot CO \cdot NMe \cdot NH_2$, in the form of its benzylidene derivative,

$$CHPh{:}N \cdot NMe \cdot CO \cdot CO \cdot NMe \cdot N{:}CHPh,$$

m. p. 210° (compare Backer, T., 1912, **101**, 594) and at the same time a small amount of another benzylidene derivative was isolated, probably coming from the mixed *aβ*-hydrazide, $NH_2 \cdot NMe \cdot CO \cdot CO \cdot NH \cdot NHMe$. Of the symmetrical disubstituted hydrazines two were examined. *s*-Dimethylhydrazine hydrochloride gave with oxalyl chloride a *compound*, $C_8H_{12}O_4N_4$, not melting at 365° and probably having the constitution $\begin{matrix} CO \cdot NMe \cdot NMe \cdot CO \\ | \qquad\qquad | \\ CO \cdot NMe \cdot NMe \cdot CO \end{matrix}$. The principal product of the interaction of *s*-dibenzoylhydrazine and oxalyl chloride was diphenyl-1 : 3 : 4-oxadiazole, $CPh\langle \begin{matrix} N \cdot N \\ O \end{matrix} \rangle CPh$, m. p. 139—140° (compare Pinner, *Ber.*, 1894, **27**, 100; Stollé, A., 1904, i, 453). At the same time, a small amount of a crystalline *compound*, $C_{16}H_{10}O_4N_2$, m. p. 168—170°, was obtained, but its constitution not determined.

Three unsymmetrical disubstituted hydrazines were examined:—*as*-Dimethylhydrazine hydrochloride yielded with oxalyl chloride oxalyl-bis-*β*-dimethylhydrazide, $NMe_2 \cdot NH \cdot CO \cdot CO \cdot NH \cdot NMe_2$, m. p. 233° (compare Backer, A., 1912, i, 730). Phenylmethylhydrazine similarly yielded *oxalyl-bis-β-phenylmethylhydrazide*,

$$NMePh \cdot NH \cdot CO \cdot CO \cdot NH \cdot NMePh,$$

m. p. 196—197°, giving in solution in strong sulphuric acid with oxidising agents an intense red colour. as-Diphenylhydrazine with oxalyl chloride yielded *oxalyl-bis-β-diphenylhydrazide*,

$$NPh_2 \cdot NH \cdot CO \cdot CO \cdot NH \cdot NPh_2,$$

decomposing at 335—336°. With these three hydrazides the solubility diminishes as the methyl groups are replaced by phenyl groups. These

three hydrazides were then used as mixed tertiary derivatives of hydrazine and submitted to the action of oxalyl chloride. Oxalyl-bis-β-dimethylhydrazide with oxalyl chloride gave a yellow *compound*, $C_8H_{12}O_4N_4$, m. p. 238—240°, which was readily decomposed by water, giving for each molecule one molecule of carbon monoxide and one of carbon dioxide, and leaving in the aqueous solution the original hydrazide. With 1 : 3 : 4-tolylenediamine in absolute alcohol the compound yielded on boiling 2 : 3-dihydroxy-6-toluquinoxaline (compare Hinsberg, A., 1887, 382; Meyer, A., 1897, i, 376). On prolonging the heating of these two substances together dimethylhydrazine was obtained. As a result of these reactions the author considers this compound to be a mono-dimethylosazone of oxalic anhydride and to have the constitution $\begin{matrix}CO\cdot O\cdot C{:}N\cdot NMe_2\\ |\\ CO\cdot O\cdot C{:}N\cdot NMe_2\end{matrix}$. Oxalyl-bis-$\beta$-phenylmethylhydrazide with oxalyl chloride yields a deep red, crystalline *compound*, $C_{18}H_{16}O_4N_4$, m. p. 229—230° (decomp.). This compound is also decomposed by water, giving carbon monoxide and carbon dioxide, and gives with tolylenediamine 2 : 3-dihydroxy-6-toluquinoxaline, and, on prolonging the heating, phenylmethylhydrazine. It is therefore considered to be the monophenylmethylosazone of oxalic anhydride, $\begin{matrix}CO\cdot O\cdot C{:}N\cdot NMePh\\ |\\ CO\cdot O\cdot C{:}N\cdot NMePh\end{matrix}$. Oxalyl-bis-$\beta$-diphenylhydrazide did not react with oxalyl chloride in benzene even on boiling for several days, or on the addition of catalysts such as cuprous chloride or pyridine. Oxalyl chloride reacted with the hydrochloride of ethyl hydrazinoacetate in benzene, giving a *compound*, $(C_3H_4O_2N)_n$, which could not be obtained crystalline, and of which the molecular weight could not be determined.

Chloroacetyl chloride reacted with *as*-phenylmethylhydrazine hydrochloride in benzene, giving *chloroacetylphenylmethylhydrazide*,

$$C_9H_{11}ON_2Cl,$$

needles, m. p. 75°, which with alcoholic potassium hydroxide gave *bis-phenylmethylaminodiketopiperazine*,

$$NMePh\cdot N\begin{matrix}CO\cdot CH_2\\ CH_2\cdot CO\end{matrix}N\cdot NMePh,$$

m. p. 244—245° (compare Abenius, *J. pr. Chem.*, 1897, [ii], **47**, 183). The author could not obtain sufficient of this compound to oxidise it and so obtain the corresponding tetraketopiperazine derivative.

W. G.

Hydrazides and Azoimides of Organic Acids. XXIX. Hydrazide and Azoimide of Adipic, Pimelic and *trans*-Hexahydroterephthalic Acids. Theodor Curtius (*J. pr. Chem.*, 1915, [ii], **91**, 1—38; compare A., 1914, i, 873).—An account of the conversion of adipic, pimelic, and *trans*-hexahydroterephthalic acids into tetramethylenediamine, pentamethylenediamine and *trans*-1 : 4-diamino*cyclo*hexane, by the method illustrated in the following scheme: $[CH_2]_4(CO_2Et)_2 \longrightarrow [CH_2]_4(CO\cdot NH\cdot NH_2)_2 \longrightarrow [CH_2]_4(CO\cdot N_3)_2 \xrightarrow{EtOH} [CH_2]_4(NH\cdot CO_2Et)_2 \longrightarrow [CH_2]_4(NH_2)_2$.

[With ERNST DARMSTAEDTER.]—*Adipy'dihydrazide*, $C_4H_8(CO\cdot NH\cdot NH_2)_2$, prepared by the gradual addition of ethyl adipate to boiling hydrazine hydrate (4 mols.), crystallises in lustrous leaflets, m. p. 171° and forms, with alcoholic hydrogen chloride, a *hydrochloride*, B,2HCl, m. p. 275° (decomp.). When shaken with benzaldehyde in aqueous solution, it yields a *dibenzylidene* derivative, $C_4H_8(CO\cdot NH\cdot N{:}CHPh)_2$, which crystallises in microscopic needles, m. p. 215—216°, and forms a *silver* salt, $C_{20}H_{20}O_2N_4Ag_2$, m. p. 175—176° (decomp.); the *di*-p-*hydroxybenzylidene* derivative has m. p. 275°; the *dicinnamylidene* derivative, m. p. 231—232°. *Adipyldiisopropylidenehydrazide*, $C_4H_8(CO\cdot NH\cdot N{:}CMe_2)_2$, prepared by heating the dihydrazide in acetone solution, forms a white powder, m. p. 174°.

Ethyl adipyldihydrazidediacetoacetate, $C_4H_8(CO\cdot NH\cdot N{:}CMe\cdot CH_2\cdot CO_2Et)_2$, has m. p. 125°.

When shaken with benzoyl chloride and aqueous sodium hydroxide the dihydrazide yields a *dibenzoyl* derivative, $C_4H_8(CO\cdot NH\cdot NHBz)_2$, crystallising in microscopic needles, m. p. 240°, and on treatment with iodine in alcoholic solution is converted into sec-*adipylhydrazide*, $C_4H_8\begin{<}{CO\cdot NH \atop CO\cdot NH}$, a white powder, m. p. above 300°.

Adipyldiazoimide, $C_4H_8(CO\cdot N_3)_2$, is obtained as a yellow oil by the gradual addition of hydrochloric acid to an aqueous solution of the dihydrazide and sodium nitrite. It has a penetrating odour, solidifies at −1° to a white, crystalline mass, and explodes when heated either alone or in the presence of water. In ethereal solution it reacts with *p*-toluidine and with aniline yielding the corresponding *di*-p-*toluidide*, $C_4H_8(CO\cdot NH\cdot C_6H_4Me)_2$, microscopic needles, m. p. 216°, and *anilide*, m. p. 233° respectively.

Ethyl tetramethylene-αδ-dicarbamate, $C_4H_8(NH\cdot CO_2Et)_2$, prepared by heating adipyldiazoimide in alcoholic solution, crystallises in long, slender needles, m. p. 85—86°, and on hydrolysis with hydrochloric acid is converted into tetramethylenediamine, which was characterised by means of its hydrochloride and platinichloride.

Adipyldiglycine, $C_4H_8(CO\cdot NH\cdot CH_2\cdot CO_2H)_2$, obtained by the interaction of adipylazoimide and glycine in the presence of aqueous sodium hydroxide, crystallises in prisms, m. p. 190°, and gives a deep blue coloration with potassium hypochlorite and phenol; the *ammonium* salt, m. p. 205° (decomp.), *silver* salt, m. p. about 227° (decomp.), with previous darkening at 220°, *ethyl* ester, m. p. about 60°, and *amide*, m. p. 132°, are described. Hippuric acid may be prepared from benzoylazoimide and glycine in a similar manner.

[With HANS PRINGSHEIM.]—Ethyl pimelate reacts with boiling hydrazine hydrate, yielding *pimelyldihydrazide*, $CH_2([CH_2]_2\cdot CO\cdot NH\cdot NH_2)_2$, m. p. 182°, which forms a *picrate*, crystallising in small, yellow leaflets, m. p. 166°; the *dibenzylidene* derivative, $C_5H_{10}(CO\cdot NH\cdot N{:}CHPh)_2$ has m. p. 185°; the *di*-p-*hydroxybenzylidene* derivative, m. p. 210°. The dihydrazide yields a *dibenzoyl* derivative, m. p. 211°, and when

heated with acetone forms a *diisopropylidene*, $C_5H_{10}(CO\cdot NH\cdot N{:}CMe_2)_2$, m. p. 129°. On treatment with nitrous acid in aqueous solution it is converted into *pimelyldiazoimide*, $C_5H_{10}(CO\cdot N_3)_2$, which forms an explosive oil and reacts with *p*-toluidine in ethereal solution, yielding *pimelo-p-toluidide*, lustrous leaflets, m. p. 206°.

Ethyl pentamethylenedicarbamate, $C_5H_{10}(NH\cdot CO_2Et)_2$, prepared by boiling an alcoholic solution of pimelyldiazoimide, has m. p. 71° and is hydrolysed by hydrochloric acid to pentamethylenediamine, of which the hydrochloride and *platinichloride* were analysed.

Succinyldiglycine, $C_2H_4(CO\cdot NH\cdot CH_2\cdot CO_2H)_2$, obtained by shaking succinyldiazoimide with glycine in the presence of aqueous sodium hydroxide, crystallises in microscopic, transparent columns, m. p. 205°, and forms an *ammonium* salt, m. p. 184°, containing $1H_2O$; the *silver*, *magnesium*, *copper*, and *barium* salts are also mentioned; the *ethyl* ester, prepared from the silver salt and ethyl iodide, crystallises in slender needles, m. p. 116°, and on treatment with aqueous ammonia is converted into *succinyldiglycinamide*, m. p. 234°.

[With Richard Stangassinger.]—Methyl *trans*-hexahydroterephthalate reacts with hydrazine hydrate in boiling alcoholic solution, yielding trans-*hexahydroterephthaloylhydrazide*, $C_6H_{10}(CO\cdot NH\cdot NH_2)_2$, which crystallises in slender, strongly anisotropic needles of high m. p. and forms a *hydrochloride*, crystallising in slender needles; the *dibenzylidene*, $C_6H_{10}(CO\cdot NH\cdot N{:}CHPh)_2$, and *di-o-hydroxybenzylidene* derivatives are white powders, m. p. above 300°. The *diisopropylidene* derivative, $C_6H_{10}(CO\cdot NH\cdot N{:}CMe_2)_2$, crystallises in clusters of very slender needles; the derivative from ethyl acetoacetate,

$$C_6H_{10}(CO\cdot NH\cdot N{:}CMe\cdot CH_2\cdot CO_2Et)_2,$$

forms a white powder, m. p. above 300°.

The hydrazide reacts with aqueous potassium cyanate, yielding trans-*hexahydroterephthaloyldisemicarbazide*,

$$C_6H_{10}(CO\cdot NH\cdot NH\cdot CO\cdot NH_2)_2,$$

which separates in white, granular, doubly refractive crystals of cubical appearance, m. p. above 300°. On treatment with sodium nitrite and acetic acid in aqueous solution, it is converted into trans-*hexahydroterephthaloyldiazoimide*, $C_6H_{10}(CO\cdot N_3)_2$, crystallising in soft, colourless needles, m. p. 63°. When kept for several days the crystals of the azoimide lose their transparency and then have m. p. about 55°. This change is probably due to the transformation of the azoimide into the *dicarbimide*, $C_6H_{10}(N{:}C{:}O)_2$.

Ethyl-trans-*hexahydrophenylene*-1 : 4-*dicarbamate*, $C_6H_{10}(NH\cdot CO_2Et)_2$, prepared by heating the azoimide in alcoholic solution, crystallises in lustrous, anisotropic needles of prismatic habit, m. p. 236°; the *methyl* ester, m. p. 263°, and *benzyl* ester, lustrous, anisotropic columnar needles, m. p. 244—245°, were prepared in a similar manner.

When heated with aniline at 200° the azoimide yields the *dicarbamide*, $C_6H_{10}(NH\cdot CO\cdot NHPh)_2$, as a white mass which chars without melting; if the reaction with aniline is carried out in ethereal solution at the ordinary temperature, a yellow *substance*,

$$CO(NH\cdot C_6H_{10}\cdot NH\cdot CO\cdot NHPh)_2,$$

insoluble in all solvents, is produced. The latter substance is accom-

panied by a small amount of a white, amorphous *anilidecarbamide*, $NHPh{\cdot}CO{\cdot}C_6H_{10}{\cdot}NH{\cdot}CO{\cdot}NHPh$, m. p. above 300°, which is readily separated by taking advantage of its solubility in alcohol.

When boiled with water for seven hours, the azoimide is converted into the *substance*, $CO(NH{\cdot}C_6H_{10}{\cdot}NH{\cdot}CO_2H)_2$, whilst, if the heating is more prolonged, a cyclic *dicarbamide*, $CO<^{NH{\cdot}C_6H_{10}{\cdot}NH}_{NH{\cdot}C_6H_{10}{\cdot}NH}>CO$, is produced. Both substances are insoluble in all organic media and show no m. p. trans-1 : 4-*Diamino*-cyclo-*hexane*, prepared by the hydrolysis of ethyl *trans*-hexahydrophenylene-1 : 4-dicarbamate with concentrated hydrochloric acid at 120°, has b. p. 87—88°/18 mm., and crystallises in long, slender columns, m. p. 56—58° ; the *hydrochloride*, $C_6H_{10}(NH_2)_2,2HCl$, small, lustrous leaflets, *platinichloride*, *aurichloride*, yellow, slender, anisotropic columns, which decompose without melting, *picrate*, lustrous anisotropic, citron-yellow leaflets, and *sulphate* are described ; the *dibenzoyl* derivative has m. p. above 300°. The oily 1 : 4-diamino*cyclo*-hexane described by Baeyer and Noyes (A., 1899, i, 1147) probably consists of a mixture of the *cis*- and *trans*-isomerides. F. B.

The Action of Arsenite on Nitrosomethylurethane. A. Gutmann (*Ber.*, 1915, **48**, 59—62).—Having already observed that sodium benzene-diazoxide unlike the *iso*diazoxide, readily oxidises sodium arsenite to arsenate (A., 1912, i, 397), the author has submitted diazomethane, ethyl diazoacetate and nitrosomethylurethane to the action of an alkaline solution of sodium arsenite. In the case of the former two substances no formation of arsenate was observable but with the last named a sufficiently concentrated solution of arsenite underwent oxidation.

The oxidation of the arsenite in this case is attributed to the primary formation of sodium methyl diazoxide in which the author regards the oxygen atom as especially reactive. D. F. T.

Azibutanone. I. Otto Diels and Karl Pflaumer. (*Ber.*, 1915, **48**, 223—231).—The reaction between diacetyl and hydrazine leads to numerous products, including complex azines. These may be derived from the simple monohydrazone, which has the normal structure, $CH_3{\cdot}CO{\cdot}CMe{:}N{\cdot}NH_2$, for it condenses with benzaldehyde and forms an acetyl compound. On oxidation, it yields azibutanone, $CH_3{\cdot}CO{\cdot}CMe{:}N_2$, which is a very reactive, orange coloured oil, losing nitrogen when treated with water, alcohol, or acids. It is not certain if it forms dimethylketen or its transformation product, tetramethyl-*cyclo*butanedione, on heating, but this may be so, for it yields *iso*-butanilide when warmed with aniline.

A mixture of hydrazine hydrate (6 grams) and water (3 c.c.) is dropped into diacetyl (10 c.c.) cooled to −20°, and the solution is then left at the room temperature. *Diacetyl monohydrazone* soon commences to separate, in colourless crystals, m. p. 67°. Large crystals are stable but the powder soon becomes yellow and the compound is very

sensitive towards dilute acids, which transform it into a yellow, amorphous substance. The *benzylidene* compound,

$$CH_3{\cdot}CO{\cdot}CMe{:}N{\cdot}N{:}CHPh,$$

forms deep yellow leaflets, m. p. 45—46°, and the *acetyl* derivative, $C_6H_{10}O_2N_2$, which may also be prepared by the action of acetylhydrazine on diacetyl, has m. p. 163°.

When a suspension of the finely divided hydrazone in ice-cold water is treated with nitrous fumes, the *azine*, $(CH_3{\cdot}CO{\cdot}CMe{:}N{\cdot})_2$, is formed. The same compound may be prepared by shaking an aqueous solution of the hydrazone with diacetyl and then cooling in ice, when it soon separates in crystalline masses. It forms stout, yellow crystals, m. p. 39°, b. p. 104—109°/12 mm., which have an intense, pleasant odour of geraniums and impart deep yellow colours to organic solvents. If the mother liquor is kept for some time in the cold, a more complicated *azine*, CMeAc:N·N:CMe·CMe:N·N:CMeAc, separates. This forms colourless, brilliant scales, m. p. 105°, b. p. 144°/17 mm.

In order to oxidise the hydrazone, it is dissolved in ether and shaken with silver oxide and anhydrous sodium sulphate. The solvent is then slowly distilled from the dark orange filtrate and the residue fractionated under reduced pressure. The yield is good. *Azibutanone*, $C_4H_6ON_2$, is a mobile, deep orange liquid, b. p. 45°/12 mm., with a stupefying, ethereal odour. The olive-green vapour explodes violently when air is too quickly admitted to the distilling flask. Azibutanone gives a brisk evolution of nitrogen when warmed with methyl alcohol, and forms the *methyl ether* of *dimethyl ketol*, $CH_3{\cdot}CO{\cdot}CHMe{\cdot}OMe$, a pleasant smelling liquid, b. p. 113—114°/759 mm. Similarly, it forms dimethylketol itself when warmed with water, dimethylketol benzoate with benzoic acid, and, apparently, α-chlorobutanone with hydrochloric acid. It also reacts with aqueous formaldehyde to form α-methylacetoacetaldehyde, $CH_3{\cdot}CO{\cdot}CHMe{\cdot}CHO$, and hydroxymethylene butanone, $CH_3{\cdot}CO{\cdot}CMe{:}CH{\cdot}OH$, which will be described in another paper. J. C. W.

Mercury Compounds of Aliphatic Amines. M. Raffo and A. Scarella (*Gazzetta*, 1915, **45**, i, 123—127).—Köhler (A., 1880, 159) regarded the compound which he obtained by the interaction of ethylamine and mercuric chloride as the ethyl derivative of the white precipitate, NH_2HgCl, formed by ammonia and mercuric chloride. Since, however, it has been shown that this white precipitate has the formula NHg_2Cl,NH_4Cl, and that mercuriammonium compounds are represented by the general formula NHg_2X, Köhler's compound must be regarded as mercuriethylammonium chloride, Hg:NHEtCl. Similar compounds, especially the nitrates, may be obtained readily by the action of aliphatic amines on mercuric salts.

Mercurimethylammonium nitrate, $Hg{:}NHMe{\cdot}NO_3 + H_2O$, forms a white, microcrystalline powder and *mercuriethylammonium nitrate*, $Hg{:}NHEt{\cdot}NO_3$, microscopic, rhombic plates.

The action of an alcoholic solution of amylamine on mercuric nitrate solution yields the complex *salt*,

$$Hg{:}NH(C_5H_{11}){\cdot}NO_3 + C_5H_{11}{\cdot}NH_2,HNO_3,$$

as a white, microcrystalline precipitate. When treated with 2% sodium hydrogen carbonate solution, this double salt is converted into free *mercuriamylamine*, $Hg{:}N{\cdot}C_5H_{11}$, which forms a white powder.

Mercurimethylammonium chloride, Hg:NHMeCl, forms a white microcrystalline precipitate. T. H. P.

Preparation of Mercurised Amino-compounds. J. D. Riedel (D.R.-P., 279,199; from *J. Soc. Chem. Ind.*, 1915, **34**, 250).—The alkali salts of aminomethanedisulphonic acid are treated with mercuric oxide in presence of water. The aqueous solutions of the compounds, if mixed with a little alkali carbonate and protected from the air, are quite stable and may be used for injections. They do not precipitate albumin. J. C. W.

The Replacement of Substituents in Benzene Derivatives. A. F. Holleman (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1027—1034).—As a corollary to his studies on the introduction of substituents into the benzene nucleus, Holleman is investigating the rules governing the replacement of substituents. How great is the problem will be realised when it is pointed out that, taking 14 common substituents, there are theoretically possible 315 di-derivatives and 4774 tri-derivatives. Of these, only 130 of the former and 232 of the latter have been tested as to the replacement of their substituents, and this for so many different purposes that the results are valueless for a systematic study.

At the outset, three points have been tested; (1) the velocity of transformation in a complete set of isomerides, (2) the effect of changing the reacting agent, and (3) the effect of temperature. If the influence of position, of the reagent, and of temperature on the velocity constant followed any definite rule the study of the replacement of a given substituent in a whole series of compounds would be simplified, but, as the experiments show, this is by no means the case.

The 3 dichlorobenzenes, 3 chloronitrobenzenes and 6 dichloronitrobenzenes have as yet been studied, with regard to the replacement of chlorine by sodium methoxide and diethylamine. As the details will be published in the *Rec. trav. chim.* (with de Mooy), it may be as well to give only the conclusions at this point. It has been found that the replacement of chlorine is largely dependent on the position of the substituents, and influenced by the reagent employed, and that, although the temperature coefficient is fairly constant for one set of isomerides and one reagent, it is not the same for the two reagents, the reaction with sodium methoxide being influenced much more than the reaction with diethylamine. J. C. W.

Some Nitro- and Halogen Derivatives of ψ-Cumene. A. Huender (*Rec. trav. chim.*, 1915, **34**, 1—33).—The author has prepared trinitro-ψ-cumene, m. p. 185°, by nitrating ψ-cumene with a mixture of nitric and sulphuric acids and has submitted the nitro-compound to the action of a number of reagents. To prove the constitution of some of the products he has prepared a number of nitro-, bromo- and chloro- derivatives of ψ-cumene.

With sodium methoxide in alcohol trinitro-ψ-cumene yields 6-*methoxy*-3 : 5-*dinitro*-ψ-*cumene*, m. p. 80°, and sodium nitrite. A similar reaction took place with sodium ethoxide, but the ethoxy-derivative could not be isolated owing to resinification. Similarly, with aqueous sodium hydroxide acting on an acetone solution of trinitro-ψ-cumene, the formation of sodium nitrite was demonstrated but the dinitro-ψ-cumenol could not be isolated. When heated with alcoholic ammonia in a sealed tube at 120—130°, trinitro-ψ-cumene gave 3 : 5-*dinitro*-6-ψ-*cumidine*, m. p. 183°. With an alcoholic solution of methylamine, 3 : 5-*dinitro*-6-*methylamino*-ψ-*cumene*, m. p. 140°, was obtained, which with nitric acid (D 1·52) gave 3 : 5-*dinitro*-6-*methylnitroamino*-ψ-*cumene*, m. p. 113°. Attempts to replace the 6-nitro-group by an ·SH group by the action of sodium sulphide on trinitro-ψ-cumene, only yielded nitro-ψ-cumidinesulphonic acid owing to intramolecular oxidation (compare Blanksma, A., 1905, i, 425). This difficulty was overcome by adding sodium sulphide in alcoholic solution to 4-chloro-1 : 3-dinitrobenzene in the same solvent, filtering the resulting liquid, and adding the filtrate to an alcoholic solution of trinitro-ψ-cumene, when 4 : 6 : 2′ : 4′-*tetranitro*-2 : 3 : 5-*trimethyldiphenyl sulphide*, m. p. 215°, was obtained.

To confirm the supposition that it was the 6-nitro-group in trinitro-ψ-cumene which was so readily replaceable the following preparations were made. The three bromo-ψ-cumenes were prepared as follows. 5-Bromo-ψ-cumidine hydrobromide was diazotised and the solution poured on to a boiling solution of cuprous bromide in hydrobromic acid, giving 5-*bromo*-ψ-*cumene*, m. p. 72°. This substance was also obtained by the direct bromination of ψ-cumene in the presence of powdered iron, and at the same time an oil, b. p. 226—230°, was obtained, which was a mixture of 3- and 6-bromo-ψ-cumenes. To prepare 3-bromo-ψ-cumene in the pure state, 3-nitro-ψ-cumene was reduced by iron in sulphuric acid and the resulting 3-ψ-*cumidine*, b. p. 235°/760 mm., diazotised and submitted to the Sandmeyer reaction, 3-*bromo*-ψ-*cumene* being obtained as an oil. 6-*Bromo*-ψ-*cumene* was obtained as an oil, b. p. 223°/760 mm., by similar treatment of 6-ψ-cumidine (compare Auwers, A., 1886, 143). A better yield of 6-bromo-ψ-cumene was obtained by brominating 5-ψ-cumidine in concentrated hydrochloric acid, and diazotising the resulting 6-*bromo*-5-ψ-*cumidine*, m. p. 72°, and eliminating the amino-group, the product being the required 6-bromo-ψ-cumene. 6-Bromo-5-ψ-cumidine, on boiling with acetic anhydride, gives an *acetyl* derivative, m. p. 204°, which with nitric acid (D 1·52) yields 6-*bromo*-3-*nitro*-5-*aceto*-ψ-*cumidide*, m. p. 235°; the latter on hydrolysis with concentrated sulphuric acid yielded 6-bromo-3-nitro-5-ψ-cumidine, m. p. 150° (compare Blanksma, loc. cit.).

Of the dinitro-ψ-cumenes only 3 : 6-dinitro-ψ-cumene, m. p. 96°, was previously known (compare Nietzki, A., 1894, i, 406). The author has now prepared the other two. 3 : 5-*Dinitro*-ψ-*cumene*, m. p. 72°, was prepared by diazotisation and the Sandmeyer reaction, from 3 : 5-dinitro-ψ-cumidine (see above). For the third isomeride 3-ψ-cumidine was acetylated and then nitrated with a mixture of sulphuric and

nitric acids giving 5 : 6-*dinitro*-3-*aceto*-ψ-*cumidide*, yellow crystals, m. p. 221°, which on hydrolysis yielded 5 : 6-*dinitro*-ψ-*cumidine*, m. p. 206°, and this by diazotisation gave 5 : 6-*dinitro*-ψ-*cumene*, yellow crystals, m. p. 90°. 3 : 5-Dinitro-ψ-cumene, on reduction with alcoholic ammonium sulphide, yielded 3-nitro-5-ψ-cumidine (compare Mayer, A., 1887, 659, 953) and 3 : 6-dinitro-ψ-cumene, when similarly reduced, gave 3-*nitro*-6-ψ-*cumidine*, m. p. 92°, which with bromine in acetic acid yielded 5-*bromo*-3-*nitro*-6-ψ-*cumidine*, m. p. 165°.

The three isomeric bromodinitro-ψ-cumenes have been obtained by nitrating the corresponding bromo-ψ-cumenes ; 5-*bromo*-3 : 6-*dinitro*-ψ-*cumene* has m. p. 218° ; 3-*bromo*-5 : 6-*dinitro*-ψ-*cumene*, m. p. 180°, and 6-*bromo*-3 : 5-*dinitro*-ψ-*cumene*, m. p. 179°.

6-*Chloro*-ψ-*cumene* was obtained as an oil, b. p. 210°/760 mm., by the Sandmeyer reaction from 6-ψ-cumidine, and on nitration yielded 6-*chloro*-3 : 5-*dinitro*-ψ-*cumene*, m. p. 162°.

Although the 6-nitro-group in trinitro-ψ-cumene can be easily replaced as already shown, the chlorine in 6-chloro-3 : 5-dinitro-ψ-cumene is only with difficulty replaced by heating with alcoholic ammonia, and 6-bromo-3 : 5-dinitro-ψ-cumene is not acted on under such conditions. Furthermore, in the case of 5-bromo-3 : 6-dinitro-ψ-cumene neither the bromine nor the 6-NO_2 group are at all readily attacked by the agents previously indicated and 3-bromo-5 : 6-dinitro-ψ-cumene gives negative results under the same conditions.

A peculiar reaction has been noted with a mixture of sulphuric and nitric acids on certain of these haloid-dinitro-ψ-cumenes, a product being obtained which contains a nitro-group very easily replaceable by other groups. 5-Bromo-3 : 6-dinitro-ψ-cumenes, when dissolved in nine times its weight of nitric acid (D 1·52) heated on a water-bath and to the liquid added an equal volume of sulphuric acid (D 1·82) yielded a *compound*, $C_9H_8O_7N_3Br$, m. p. 150°, which the author provisionally terms a nitrate. 5-Chloro-3 : 6-dinitro-ψ-cumene gave a *compound*, m. p. 147°, and 6-bromo-3 : 5-dinitro-ψ-cumene a *compound* m. p. 185°, whilst 3-bromo-5 : 6-dinitro-ψ-cumene, and trinitro-ψ-cumene were not acted on under such conditions. The compound from 5-bromo-3 : 6-dinitro-ψ-cumene has been examined in detail. On heating it with water alone, or better with water and acetone as a solvent, in a sealed tube, a crystalline *compound*, $C_9H_9O_5N_2Br$, m. p. 202°, was obtained, whilst the aqueous liquid gave the tests for nitrites. The same compound was obtained by acting on the nitrate with sodium methoxide or ethoxide in alcohol or with alcoholic ammonia ; the two former reagents yielded, however, a second crystalline *compound*, m. p. 190°. On heating the nitrate in alcoholic solution with methylamine, a *compound*, $C_{10}H_{12}O_4N_3Br$, crystallising in colourless needles, m. p. 185°, was obtained, while if ethylamine was used a *compound*, $C_{11}H_{14}O_4N_3Br$, m. p. 130°, was obtained. The compound obtained with methylamine on solution in nitric acid lost nitrogen and gave the compound, m. p. 190°, obtained from the nitrate with alcoholic ammonia. On boiling the nitrate with aniline, a yellow, crystalline *compound*, $C_{15}H_{14}O_4N_3Br$, m. p. 168°, was obtained. The author considers that the compound he calls a nitrate is either (1) a substance containing a nitro-group in

the side chain, with a group $\cdot CH_2 \cdot NO_2$ or (2) an additive product of bromodinitro-ψ-cumene and nitric acid, or (3) a nitrate of bromodinitro-ψ-cumene, and containing the group $\cdot CH_2 \cdot O \cdot NO_2$. W. G.

The Synthesis of *p*-Thiol-β-phenylethylamine. HAROLD KING (T., 1915, **107**, 222—230).—Benzo-*p*-amino-β-phenylethylamide,

$$NH_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NHBz,$$

is readily converted by diazotisation and treatment with potassium xanthate in alkaline solution into benzo-*p*-xanthyldiazo-β-phenylethylamide, which, at 70°, passes spontaneously into *benzo*-p-*xanthyl-β-phenylethylamide*, $COSEt \cdot S \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NHBz$. The latter is converted by hydrolysis into *benzo-p-thiol-β-phenylethylamide*, which is very susceptible to oxidising agents. For the isolation of p-*thiol-β-phenylethylamine* from it, the most practical way is to convert it by oxidation into the *disulphide*, $S_2(C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NHBz)_2$, which, when hydrolysed with hydrochloric acid, yields the di*hydrochloride* of *di-β-phenylethylamine* p-*disulphide*, $S_2(C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NH_2,HCl)_2$. On reduction with tin and hydrochloric acid, the latter gives the *hydrochloride* of p-*thiol-β-phenylethylamine*.

All the thiol compounds and disulphides obtained give the coloration described by Johnson and Brautlecht (A., 1912, i, 805) for thioltyrosine and its disulphide. Unlike tyrosine and *p*-hydroxyphenylethylamine, the characteristic reaction with Mörner's reagent is not shown by *p*-thiol-β-phenylethylamine or any of its derivatives.

With regard to physiological activity, *p*-thiol-β-phenylethylamine is found to have about one-sixth the pressor activity and the disulphide one-thirtieth the activity, of *p*-hydroxy-β-phenylethylamine.

Benzo-*p*-amino-β-phenylethylamide, m. p. 133·5—134·5° (corr.), [Barger and Walpole, T., 1909, **95**, 1722, give 134°] is prepared by the reduction of benzo-*p*-nitro-β-phenylethylamide by tin and hydrochloric acid. The hydrochloride, hexagonal leaflets, has m. p. 283—285° (corr.) [Barger and Walpole give m. p. above 280° (decomp.)], the *sulphate*, six-sided leaflets, melts at 278—279° (corr. decomp.) whilst the *acetyl* derivative, rectangular leaflets, has m. p. 209·5—210·5° (corr.). When the base is diazotised and the diazo-solution treated with potassium xanthate, benzo-*p*-xanthyldiazo-β-phenylethylamide separates as a bright yellow cloud which rapidly passes into benzo-*p*-xanthyl-β-phenylethylamide. Boiling, aqueous alcoholic potassium hydroxide solution converts the latter into a mixture of benzo-*p*-thiol-β-phenylethylamide, m. p. 133—136°, and dibenzo-di-β-phenylethylamide *p*-disulphide, minute needles, m. p. 199—201° (corr.). Oxidation of benzo-*p*-thiol-β-phenylethylamide by potassium ferricyanide solution readily yields the latter compound, which on treatment with 20 per cent. aqueous hydrochloric acid at 150° passes into di-β-phenylethylamine *p*-disulphide dihydrochloride, hexagonal leaflets, m. p. 339·5—340·5° (corr. decomp.). The *sulphate* crystallises readily but the *picrate* and *styphnate* are oily; the free *base* is an almost colourless oil which, on exposure to air, readily forms a crystalline *carbonate*.

Di-β-phenylethylamine *p*-disulphide dihydrochloride is reduced by tin foil and hydrochloric acid in the presence of alcohol to *p*-thiol-β-

phenylethylamine hydrochloride, glistening leaflets, m. p. 231·5—233 (corr.). The corresponding free *base* is obtained by cautious addition of sodium hydroxide to an aqueous solution of the hydrochloride. It forms hexagonal leaflets, m. p. 216—217° (corr.). The *picrate*, orange-yellow needles, has m. p. 156·5—157·5° (corr. decomp.). H. W.

The Behaviour of Phenols and Phenolic Ethers with Unsaturated Side Chains towards Ozone. C. HARRIES and R. HAARMANN (*Ber.*, 1915, **48**, 32—41).—The earlier results obtained in the formation and fission of the ozonides of unsaturated phenols such as eugenol are not entirely satisfactory (compare Harries and Weiss, A., 1904, i, 861), because under the usual conditions the normal course of the changes is considerably disturbed by complications. The problem has therefore been re-examined in the case of the substances detailed below, of which it was found generally possible to prepare the ozonides by treatment of a solution with a well-dried 1% ozone.

In hexane solution *iso*eugenol gave a yellow, syrupy *ozonide*, $C_{10}H_{12}O_5$, which, when produced in acetic acid solution, underwent decomposition, giving acetaldehyde and a 25—38% yield of vanillin together with resinous substances. It was found that mere treatment of an acetic acid solution of *iso*eugenol with a current of oxygen for 120 hours also effects partial oxidation to vanillin, this substance being produced to the extent of approximately 12%. By reducing *iso*eugenol ozonide in ethereal solution by means of zinc dust and acetic acid (compare Harries, A., 1905, i, 225; 1906, i, 833), vanillin could be obtained to the extent of 71% of the theoretical yield.

*iso*Eugenyl acetate is remarkable in combining with more than the expected proportion of ozone, the ozonide produced in ethyl acetate solution being a crystalline solid of the composition $C_{12}H_{14}O_9$. On fission with acetic acid, this ozonide gives rise to acetylvanillic acid in poor yield.

Eugenol ozonide, obtained by the action of 1% ozone on a solution of eugenol in ethyl acetate, is an oily substance which is considerably more explosive than *iso*eugenol ozonide. When decomposed by warming with acetic acid, no formation of homovanillin is observable, the only product being a brown *oil*, b. p. 120—200°/0·5 mm., which rapidly resinifies. Reduction of eugenol ozonide in ethereal solution by means of zinc dust and acetic acid caused fission with formation of *homovanillin*, $OMe{\cdot}C_6H_3(OH){\cdot}CH_2{\cdot}CHO$, a colourless, viscous oil b. p. 111—114°/0·45 mm., with a smell resembling vanilla; *p-nitrophenylhydrazone*, deep yellow needles, m. p. 150°; *semicarbazone*, prisms, m. p. 173°; *oxime*, leaflets or needles, m. p. 115°; *bisulphite compound*, colourless powder.

Eugenyl acetate, in contrast to *iso*eugenyl acetate, forms a normal *ozonide*, $C_{12}H_{14}O_6$, which is conveniently obtained by the action of 1% ozone on a solution in hexane; the ozonide separates from ethereal solution in colourless tablets or needles, m. p. 63°. Fission of the ozonide by acetic acid produces acetylhomovanillic acid, acetylhomovanillin, and vanillin, the presence of the last-named being probably due to the intermediate formation of a non-isolatable peroxide of homo-

vanillin, e.g. $OMe\cdot C_6H_3(OH)\cdot CH_2\cdot CH<\begin{matrix}O\\|\\O\end{matrix}$, which subsequently decomposes with a slight simultaneous rearrangement, giving formaldehyde and vanillin.

Eugenol methyl ether ozonide (Majima, A., 1909, i, 945), on fission by acetic acid, gave methylvanillin as the only isolatable product. Reduction of the ozonide yielded a yellow liquid, b. p. 112—113°/0·6 mm., of which a preliminary examination indicated it to be *methylhomovanillin* (p-*nitrophenylhydrazone*, m. p. 157°; *semicarbazone*, m. p. 181°). This substance, however, is to be further examined.

The above results provide an explanation for the contradictory results of earlier investigators, who have found it possible to obtain vanillin from *iso*eugenol, using oxygen relatively poor in ozone, whilst later investigators with more effective ozone apparatus at their disposal applied too concentrated ozone and obtained only resinous products. D. F. T.

Nitroguaiacols. David Cardwell and Robert Robinson (T., 1915, **107**, 255—259).—The isomeric nitroguaiacols may be obtained by hydrolysis of nitroveratrole, alkaline reagents converting the methoxy-group in the *para*-position with respect to the nitro-group into hydroxyl, and so producing 4-nitroguaiacol, whereas acid hydrolysis affects the *meta*-methoxy-group and yields 5-nitroguaiacol. An interpretation according to the theories of Werner and Flürscheim is suggested. 6-Nitrohomoveratrole is not readily attacked by alkali hydroxides, but evidence is included which points to the fact that in this case also hydrobromic acid hydrolyses the methoxy-group in the *meta*-position with respect to the nitro-group.

5-Nitroguaiacol, m. p. 104—105°, is produced by heating nitroveratrole with concentrated hydrobromic acid at 98°; larger quantities of acid yield nitrocatechol. When the monopotassium salt of the latter is heated with methyl iodide and ethyl alcohol at 100°, 5-nitroguaiacol is formed.

4-Nitroguaiacol, m. p. 101—102°, is formed when nitroveratrole is boiled with a solution of potassium hydroxide in methyl alcohol and water. Hydrolysis of this substance with hydrobromic acid yields nitrocatechol under conditions whereby nitroveratrole yields 5-nitroguaiacol and the latter compound remains unchanged.

6-*Nitro*-4-*hydroxy*-m-*tolyl methyl ether*, bright yellow prisms, m. p. 138—140° (*potassium* salt, slender, yellow needles), is obtained by heating 6-nitrohomoveratrole with glacial acetic acid and aqueous hydrobromic acid; nitrohomocatechol (compare Cousin, *Bull Soc. Chim.*, 1893, [iii], **9**, 53, 157), m. p. 180—182°, is formed as by-product. Nitration of 4-acetoxy-*m*-tolyl methyl ether in acetic acid solution gives a *product*, pale yellow, feathery needles, m. p. 138—139°, identical with that obtained by the action of acetic anhydride on the potassium salt of 6-nitro-4-hydroxy-*m*-tolyl methyl ether, and the identity is further established by the isolation of the nitrohydroxytolyl methyl ether, m. p. 138—140°, from the acetyl derivative by means of alcoholic potassium hydroxide. H. W.

4-Thiol-α-naphthol. TH. ZINCKE and J. RUPPERSBERG (*Ber.*, 1915, **48**, 120—130).—The preparation and properties of *4-thiol-α-naphthol* and of certain of its derivatives are described.

Sodium α-ethylcarbonatonaphthalene-4-sulphonate, long, almost colourless needles, is obtained by the addition of ethyl chloroformate to a well-cooled alkaline solution of sodium α-naphtholsulphonate, and is converted by warming with phosphorus pentachloride into *α-ethylcarbonatonaphthalene-4-sulphonyl* chloride, m. p. 84°. The latter is readily decomposed by alkali with regeneration of the sulphonic acid, but is very stable towards concentrated hydrochloric acid, so that the isolation of the naphtholsulphonyl chloride could not be effected. *Ethylcarbonatonaphthalene-4-sulphanilide*, m. p. 149°, is prepared by the action of aniline on the corresponding chloride and is transformed by sodium hydroxide into *α-naphthol-4-sulphanilide*, needles, m. p. 199—200°. *Ethylcarbonatonaphthalene-4-thiol*, $SH\cdot C_{10}H_6\cdot O\cdot CO_2Et$, colourless, silky needles, is obtained by the reduction of an alcoholic solution of α-ethylcarbonatonaphthalene-4-sulphonyl chloride by zinc dust and hydrochloric acid. Its *acetyl* derivative, leaflets, has m. p. 65°. It is readily oxidised by ferric chloride in glacial acetic acid solution or by sulphuric acid in acetic anhydride (less readily by hydrogen peroxide or potassium ferricyanide in alkaline solution) to the corresponding *disulphide*, fine needles, m. p. 118°. When dissolved in methyl alcohol and treated with *N*-sodium hydroxide and methyl sulphate, it gives *4-ethylcarbonato-α-naphthyl methyl sulphide*,

$$SMe\cdot C_{10}H_6\cdot O\cdot CO_2Et,$$

leaflets, m. p. 55°. Prolonged chlorination in chloroform solution transforms the latter into a brown oil; nitric acid in glacial acetic acid solution oxidises it to the sulphoxide with simultaneous formation of some nitro-sulphoxide. With the calculated quantity of bromine in chloroform solution, it yields a well-defined dibromo- additive *product*, $C_{14}H_{14}O_3Br_2S$, reddish-brown leaflets, which readily lose bromine when preserved; treatment with sodium hydrogen sulphite regenerates the methylthiol, whilst water gives the methylsulphoxide (see later). Boiling glacial acetic acid also gives the sulphoxide, but, in addition, substitution occurs and a *monobromo*-derivative of the methyl sulphide is formed. Ethylcarbonatonaphthalene methylsulphoxide, $SOMe\cdot C_{10}H_6\cdot O\cdot CO_2Et$, crystallises in leaflets or needles, m. p. 81°, and yields with hydrogen bromide in chloroform solution the dibromide described above. Oxidation with perhydrol in glacial acetic acid solution converts the methylsulphoxide into the corresponding *sulphone*, needles or prisms, m. p. 128—129°.

4-Ethylcarbonato-α-naphthyl benzyl sulphide,

$$CH_2Ph\cdot S\cdot C_{10}H_6\cdot O\cdot CO_2Et,$$

colourless, silky needles, m. p. 99°, is obtained by the action of benzyl chloride on an aqueous-alcoholic alkaline solution of α-ethylcarbonatonaphthalene-4-thiol and, when treated with chlorine in chloroform solution, eliminates benzyl or benzylidene chloride and gives a yellow oil from which a solid derivative could not be obtained, so that the corresponding aryl sulphur chloride could not be isolated. Oxidation of the sulphide in acetic acid solution by means of hydrogen peroxide yields the *sulphone*, needles, m. p. 130°.

4-Thiol-α-naphthol, $SH\cdot C_{10}H_6\cdot OH$, needles, m. p. 114°, is obtained by saponifying 4-thiolethylcarbonato-α-naphthol with aqueous sodium hydroxide in the presence of sodium sulphide. It yields a *di-acetyl* derivative, colourless needles, m. p. 77°. Saponification of the ethylcarbonato-derivative by 2*N*-sodium hydroxide in the presence of alcohol leads to the formation of the *disulphide*, $S_2(C_{10}H_6\cdot OH)_2$, needles, m. p. 152° (*di-acetyl* derivative, m. p. 112°).

4-*Methylthiol-α-naphthol*, m. p. 110°, is prepared by saponifying the corresponding ethylcarbonato-compound with alcohol and 2*N*-sodium hydroxide (*acetyl* derivative, m. p. 65°). The methyl *compound*, $C_{12}H_{12}OS$, is obtained by the action of methyl sulphate on 4-thiol-α-naphthol and forms colourless needles, m. p. 63°. 4-Methylthiol-α-naphthol gives a reddish-brown, crystalline addition *product* with bromine, which is unstable.

α-*Naphthol-4-methylsulphoxide* is obtained by saponifying the corresponding ethylcarbonato-derivative and forms colourless needles, m. p. 157° (decomp.). α-*Naphthol-4-methyl sulphone*, m. p. 227°, α-*naphthol-4-benzyl sulphide*, m. p. 105°, and α-*naphthol-4-benzylsulphone*, m. p. 210°, are prepared from the corresponding ethylcarbonato-compounds respectively. H. W.

α-Benzhydrylbenzhydrols. H. Simonis and P. Remmert (*Ber.*, 1915, **48**, 206—213).—The three isomerides in which the group $-CPh_2\cdot OH$, the so-called "benzhydryl" radicle, is introduced into a benzene nucleus of benzhydrol, have been prepared by the action of magnesium phenyl bromide on the phthalaldehydic acids in boiling anisole (compare A., 1914, i, 270, 1067).

o-Phthalaldehydic acid was dissolved in anisole, mixed with magnesium phenyl bromide and boiled under reflux for several hours. The product was decomposed by cold sulphuric acid and then freed from anisole and diphenyl by steam distillation. The remaining oil solidified on cooling and was identified as *o*-α-benzhydrylbenzhydrol, $OH\cdot CHPh\cdot C_6H_4\cdot CPh_2\cdot OH$, m. p. 156·5° (compare Guyot and Catel, A., 1905, i, 226), for it was readily condensed to triphenylphthalan (1 : 1 : 2-triphenyl-1 : 2-dihydro*iso*benzofuran), m. p. 120° (Guyot and Catel, A., 1906, i, 761). The secondary carbinol group is attacked on acetylation, or by hydrogen bromide in cold, concentrated solution in glacial acetic acid, with the formation of the *acetate*,

$$CHPhAc\cdot C_6H_4\cdot CPh_2\cdot OH,$$

m. p. 130°, and *o*-α-*bromobenzyltriphenylcarbinol*, $C_{26}H_{21}OBr$, m. p. 184° (decomp.) respectively. In a boiling solution, however, hydrogen bromide acts as a condensing agent, yielding 9 : 10-diphenylanthracene, m. p. 246° (Haller and Guyot, A., 1904, i, 650; Guyot and Catel, loc. cit.). This did not yield anthraquinone on oxidation, but *o*-dibenzoylbenzene, m. p. 148°.

Opianic acid was also treated with magnesium phenyl bromide and converted into 2-α-*benzhydryl*-5 : 6-*dimethoxybenzhydrol*,

$$OH\cdot CHPh\cdot C_6H_2(OMe)_2\cdot CPh_2\cdot OH,$$

which forms sandy crystals, m. p. 215°. This also undergoes condensation in two directions. It is converted into 1 : 1 : 3-*triphenyl-*

6 : 7-*dimethoxyphthalan*,

$$C_6H_2(OMe)_2\langle\begin{matrix}CPh_2\\CHPh\end{matrix}\rangle O,$$

m. p. 119°, by the addition of concentrated hydrochloric acid to a solution in glacial acetic acid, whereas, by shaking a dilute solution in chloroform with concentrated sulphuric acid, 1 : 2-*dimethoxy*-9 : 10-*diphenylanthracene*,

$$C_6H_2(OMe)_2\langle\begin{matrix}CPh\\CPh\end{matrix}\rangle C_6H_4,$$

is obtained. This forms colourless leaflets, m. p. 167°, and is oxidised by chromic acid to 3 : 4-*dimethoxy*-1 : 2-*dibenzoylbenzene*, $C_{22}H_{18}O_4$, pale yellow granules, m.p. 106°.

m-α-*Benzhydrylbenzhydrol* was synthesised in the same way from *iso*phthalaldehydic acid. It has m. p. 144°, and differs from the *o*-isomeride in that both hydroxyl groups are attacked on acetylation and both are replaced by bromine under the influence of hydrogen bromide in the cold, with the formation of the *diacetate*, m. p. 106°, and m-α-*bromobenzyltriphenylbromomethane*, $CHPhBr{\cdot}C_6H_4{\cdot}CBrPh_2$, respectively.

The corresponding reaction with terephthalaldehydic acid did not follow such a smooth course, for highly coloured by-products were obtained and the p-α-*benzhydrylbenzhydrol* was purified with difficulty. It is an amorphous substance, m. p. 210°, which forms p-α-*bromobenzyltriphenylbromomethane*, $C_{26}H_{20}Br_2$, m. p. 142°, when treated with hydrobromic acid. J. C. W.

Action of 1-Chloro-2 : 4-dinitrobenzene on *p*- and *m*-Aminobenzoic Acids. B. Linke (*J. pr. Chem.*, 1915, [ii], **91**, 202—212).—2 : 4-*Dinitrodiphenylamine-4'-carboxylic acid*,

$$C_6H_3(NO_2)_2{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H,$$

prepared by heating a mixture of 1-chloro-2 : 4-dinitrobenzene, *p*-aminobenzoic acid, and calcium carbonate with 50% alcohol, separates from a mixture of phenol and glacial acetic acid as a yellow powder, which remains unchanged at 225°; the *sodium* salts form cinnabar red crystals; the *calcium*, *strontium*, *silver*, *copper*, *mercuric*, *cobalt*, *nickel*, and *iron* salts are obtained as yellow or orange precipitates by the addition of the corresponding salts to an aqueous solution of the sodium salt; the *methyl* ester crystallises in microscopic orange needles, which become carmine red at 75°, light yellow at 178°, and do not fuse at the latter temperature; the *ethyl* ester, small, yellowish-red needles, becomes dark red at 72°, light yellow at 172°, and explodes when rapidly heated.

Partial reduction with aqueous sodium sulphide gives rise to 2 (or 4)-*nitro*-4 (or 2)-*aminodiphenylamine-4'-carboxylic acid*, a reddish-brown powder (decomp. 225°), of which the *sodium* salt and *hydrochloride*, yellowish-brown powder (decomp. 195°), are described. Complete reduction with tin and hydrochloric acid yields 2 : 4-*diaminodiphenylamine-4'-carboxylic acid*. This forms a white powder (decomp. 195°), which at once acquires a dark violet colour on exposure to air; the *hydrochloride*, $C_6H_3(NH_2)_2{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H,2HCl$, crystallises in white, felted needles (decomp. 175—180°). 2 : 4-*Dinitrodiphenylamine-*

3'-*carboxylic acid*, prepared from 1-chloro-2 : 4-dinitrobenzene and *m*-aminobenzoic acid by boiling with calcium carbonate and aqueous alcohol, crystallises in small, felted needles (unchanged at 225°) and yields a *sodium* salt, which crystallises with $2H_2O$ in orange leaflets and gives, with aqueous solutions of calcium, zinc, lead, and other metallic salts, yellow or orange precipitates; the *methyl* ester crystallises in felted orange needles, m. p. 126°, the *ethyl* ester in light yellow needles, m. p. 105°. Partial reduction with aqueous sodium sulphide gives rise to 2 (or 4)-*nitro*-4 (or 2)-*aminodiphenylamine*-3'-*carboxylic acid*, a reddish-brown powder (decomp. 215—218°), of which the *sodium* salt and dark green *hydrochloride* (decomp. 175—180°) are described.

Complete reduction with tin and hydrochloric acid results in the formation of 2 : 4-*diaminodiphenylamine*-3'-*carboxylic acid*, which rapidly decomposes on exposure to air and yields a *hydrochloride* as a sandy crystalline powder (decomp. 165—170°). F. B.

Reduction of Arylsulphonamides by Hydriodic Acid. EMIL FISCHER (*Ber.*, 1915, **48**, 93—102).—The value of the arylsulphonyl derivatives of organic bases and amino-acids for the isolation of this class of compound is seriously diminished by the difficulty of regenerating the original amino-compound. It is now found that hydriodic acid (with the addition of phosphonium iodide) is a convenient reagent for effecting the recovery of the parent substance, because in a closed vessel at 70—100°, concurrent reduction and fission occur which may be typified by the result with *p*-toluenesulphonamide,

$$C_6H_4Me\cdot SO_2\cdot NH_2 + 7HI = C_6H_4Me\cdot SH + NH_4I + 3I_2 + 2H_2O.$$

In a like manner the corresponding *p*-toluenesulphonanilide and *p*-toluenesulphonylglycine undergo fission, regenerating the amino-compound.

The method proves especially useful for the recovery of the optically active amino-acids from their arylsulphonyl derivatives. p-*Toluenesulphonyl*-d-*phenylalanine*, $CH_2Ph\cdot CH(CO_2H)\cdot NH\cdot SO_2\cdot C_6H_4Me$, yields *d*-phenylalanine in excellent yield and approximate optical purity, and by making use of this process *l*-tyrosine has been converted through the *p*-toluenesulphonyl compound and its methyl derivative into active *N*-methyltyrosine, which was identical with natural rhatanin.

It is of interest that, whereas the toluenesulphonyl chloride is also sensitive to hydriodic acid, the free acid and its ethyl ester resist the action of hydriodic acid under similar conditions (compare Gutmann, A., 1914, i, 395); rather unexpectedly, "saccharin" is also resistant.

There is a marked difference between the behaviour of the arylsulphonyl radicle attached to an oxygen atom, and that attached to nitrogen; thus, *di*-p-*toluenesulphonyl*-l-*tyrosine*,

$$C_6H_4Me\cdot SO_2\cdot O\cdot C_6H_4\cdot CH_2\cdot CH(CO_2H)\cdot NH\cdot SO_2\cdot C_6H_4Me,$$

colourless prisms (*sodium* salt, microscopic tetragonal plates with $2H_2O$, from water) on treatment with hydriodic acid and phosphonium iodide at 100° gives *p*-tolyl mercaptan, m. p. 43—44°, and O-p-*toluenesulphonyl*-l-*tyrosine*, colourless needles, m. p. 218° (corr. decomp.) $[\alpha]_D^{17} - 4{\cdot}58°$ in *N*-hydrochloric acid, $-11{\cdot}68°$ in *N*-sodium hydroxide solution. Methylation of the disulphonyl compound gives *di*-p-*toluene-*

sulphonyl-N-*methyltyrosine*,

$C_6H_4Me\cdot SO_2\cdot O\cdot C_6H_4\cdot CH_2\cdot CH(CO_2H)\cdot NMe\cdot SO_2.C_6H_4Me$,

needles or prisms, m. p. 162—163° (corr.), $[\alpha]_D^{21} - 25{\cdot}34°$ (in alcohol).

The striking difference between the behaviour of the free sulphonic acid and its amides extends also to the corresponding benzyl compounds. Benzylsulphonic acid is not reduced, whereas its amide enters into reaction, readily giving, however, benzyl iodide and hydrogen sulphide in addition to ammonia. D. F. T.

Behaviour of Phenols, Naphthols, and their Carboxylic Acids towards Quadrivalent Titanium. II. O. HAUSER and A. LEVITE. (*Ber.*, 1915, **48**, 213—220; compare A., 1912, i, 847).—The pyridine salt of the dititanisalicylic acid, or, more correctly, oxydititanihexasalicylic acid, has been prepared in order to determine the molecular weight.

Stable salts of a different type, namely, of phenoltitanic acid, have also been prepared from phenols in which there are at least two neighbouring hydroxyl groups.

The constitution and stability of these complex acids is dicussed from the point of view of the Abegg-Bodländer theory of complexes and the connexion of the phenoltitanic acids with the mordant dyes in the sense of Liebermann's theories (A., 1902, i, 475; 1903, i, 510) is pointed out.

The pale yellow *pyridine* salt of *oxydititanihexasalicylic acid*, $OTi_2(O\cdot C_6H_4\cdot CO_2H)_6,4C_5NH_5$, and the yellow *pyridine* salt of *oxydititanihexa-β-hydroxynaphthoic acid*, $OTi_2(O\cdot C_{10}H_6\cdot CO_2H)_6,4C_5NH_5$, were prepared by precipitating a solution of the organic acid in a slight excess of pyridine with the calculated quantity of titanic acid (1 mol.). The molecular weight of the former was found in boiling pyridine solution.

The *aniline* salts of *catecholtitanic acid*,

$(C_6H_4O_2)_2Ti_2O(OH)_2,NH_2Ph,H_2O$,

and of *pyrogalloltitanic acid*, $(C_6H_3O_3)_2Ti_2O(OH)_2,NH_2Ph,3H_2O$, were precipitated by adding excess of aniline acetate solution to a boiling solution of the phenol and titanic acid in dilute hydrochloric acid.

J. C. W.

Diethylcarbobenzonic Acid. II. RICHARD ANSCHÜTZ and OSKAR MOTSCHMANN. (*Annalen*, 1914, **407**, 84—94; compare Anschütz and Berns, A., 1891, 913).—The reaction between magnesium, ethyl iodoacetate, and benzyl methyl ketone in benzene leads in the usual manner to the formation of *ethyl β-hydroxy-γ-phenyl-β-methylbutyrate*, $CH_2Ph\cdot CMe(OH)\cdot CH_2\cdot CO_2Et$, b. p. 162°/15 mm., which is converted by phosphorus pentachloride and subsequent distillation under diminished pressure into *ethyl γ-phenyl-β-methyl*isocrotonate,

$CHPh:CMe\cdot CH_2\cdot CO_2Et$,

b. p. 146—147°/12 mm. The acid corresponding with the latter ester reacts with concentrated hydriodic acid to form an iodobutyric acid which, in acidified alcoholic solution, is reduced by 3% sodium amalgam to *γ-phenyl-β-methylbutyric acid*, $CH_2Ph\cdot CHMe\cdot CH_2\cdot CO_2H$, a

viscous oil (*silver* salt, $C_{11}H_{13}O_2Ag$, leaflets). *γ-Phenyl-β-methylbutyryl chloride*, b. p. 133—135°/14 mm., yields an anilide, m. p. 101°, which is identical with that of the phenyl*iso*valeric acid obtained from diethylcarbobenzonic acid (*loc. cit.*). C. S.

The Acid Salts of Dibasic Acids. II. E. JUNGFLEISCH and PH. LANDRIEU (*Ann. Chim.*, 1914, [ix]. 2. 333—389). A more detailed account of work already published (compare A., 1914, i, 416.) W. G.

Synthesis of Depsides of Genistic Acid. F. MAUTHNER (*J. pr. Chem.*, 1915, ii, 91, 179—189.)—In continuation of previous work (A., 1914, i, 545) the author has prepared a number of depsides by the condensation of 3 : 6-dimethoxybenzoyl chloride with aromatic hydroxy-acids and their esters.

2 : 5-Dimethoxybenzoyl chloride has b. p. 162°/15 mm. and solidifies to a white, crystalline mass, m. p. 53—54° (compare A., 1909, i, 161); the *amide* forms colourless leaflets, m. p. 141—142°, the *anilide*, colourless needles, m. p. 98—99°.

p-2 : 5-*Dimethoxybenzoyloxybenzoic acid*, prepared by the gradual addition of an acetone solution of 2 : 5-dimethoxybenzoyl chloride to *p*-hydroxybenzoic acid dissolved in an aqueous acetone solution of sodium hydroxide at −10°, crystallises in colourless needles, m. p. 161—162°.

The following compounds were prepared in a similar manner:

Methyl p-2 : 5-*dimethoxybenzoyloxybenzoate*, from methyl *p*-hydroxybenzoate, colourless needles, m. p. 72—73°, p-2 : 5-*Dimethoxybenzoyloxy*-m-*methoxybenzoic acid*, from vanillic acid, colourless needles, m. p. 176—177°; the *methyl* ester also forms colourless needles, m. p. 113—114°, m-2 : 5-*Dimethoxybenzoyloxybenzoic acid*, from *m*-hydroxybenzoic acid has m. p. 140—141°, the *methyl* ester m. p. 81—82°.

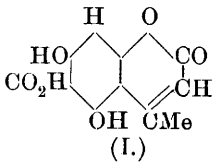
2′-2 : 5-*Dimethoxybenzoyloxy*-3′-*naphthoic acid*, prepared by the interaction of 2 : 5-dimethoxybenzoyl chloride and 2-hydroxy-3-naphthoic acid in benzene solution in the presence of quinoline, forms colourless needles, m. p. 185—186°, with previous sintering at 175°, and on treatment with diazomethane in ethereal solution is converted into the corresponding *methyl* ester, colourless needles, m. p. 150—151°.

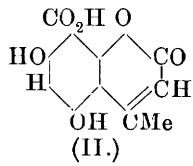
6′-2 : 5-*Dimethoxybenzoyloxy*-3′-*methoxybenzoic acid*, colourless needles, m. p. 131—132°, and 4′-2 : 5-*dimethoxybenzoyloxy*-3′ : 5′-*dimethoxybenzoic acid*, m. p. 173—174°, were prepared from the monomethyl ether of genistic acid (Graebe and Martz, A., 1905, i, 702) and syringic acid in a similar manner.

p-2 : 5-*Dimethoxybenzoyloxybenzoyl chloride*, prepared from the corresponding acid by the action of phosphorus pentachloride in chloroform solution, has m. p. 107—108°, and when shaken with α-glucose and quinoline in chloroform solution yields *penta*-(p-2 : 5-*dimethoxybenzoyloxybenzoyl*)-*glucose*, $C_{86}H_{72}O_{31}$, as an amorphous powder, m. p. 92—93°, $[\alpha]_D^{19}$ + 24·09, in acetylene tetrachloride solution.

The preparation of 2 : 5-dimethoxybenzoic acid from genistic acid is also described. F. B.

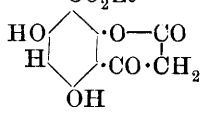
Transformations of the Ester-lactone obtained from Acetonedicarboxylic Ester and of Phloracetophenone-3-ω-dicarboxylic Ester. HERMANN LEUCHS and RUDOLF SPERLING (*Ber.*, 1915, **48**, 135—152).—In a previous communication, Leuchs and Simeon (A., 1911, i. 646) have described the isolation of an ester, $CO_2Et\cdot CH<^{CO\text{————}CH(CO_2Et)}_{CO\cdot CH(CO\cdot CH_2\cdot CO_2Et)}>CO$, as by-product in the condensation of malonic ester by sodium. Since this substance readily yields anhydrides, it seemed possible that a way was opened of preparing substances with a *para*-bridge in the benzene nucleus. The circumstances have been more fully investigated in the case of the similar but more readily prepared ester, phloracetophenone-3-ω-dicarboxylic ester, described by Jerdan (T., 1897, **71**, 1111), which, when acetylated, gives a derivative similar to the compound, $C_{23}H_{24}O_{12}$, previously described and convertible into the acid, m. p. 300—302°, to which the formula $C_9H_6O_5$ was previously ascribed. Since this acid is not esterified by alcoholic hydrogen chloride and loses carbon dioxide at 300° (or at 100° in the presence of aniline), to give a substance, $C_{10}H_8O_4$, the formula is now modified to $C_{11}H_8O_6$; it therefore appears that acetylation of the ester leads to the formation of a coumarin ring, and the acid must be represented by formula I or II, whilst the substance, $C_{10}H_8O_4$, is 5 : 7-dihydroxy-4-methylcoumarin (compare Pechmann and Cohen, A., 1885, 57).


(I.)


(II.)

The acid, $C_{15}H_{16}O_{10}$, previously described (*loc. cit.*) is also a coumarin derivative, since the acid $C_{11}H_8O_6$ can be obtained from its acetyl derivative. It loses carbon dioxide at 165° and yields ethyl phloracetophenone-3 : 5-dicarboxylate, which, on acetylation, appears to lose a molecule of water and to acquire four acetyl groups.

Jerdan's lactone has been further investigated and found to be so strongly acidic in character that it dissolves in sodium acetate solution; as a result of this observation, it has been found possible to simplify its purification and to isolate two by-products, an *isomeride* of the ester, $C_{14}H_{16}O_8$, and an *anhydride*, $C_{14}H_{14}O_7$. For the lactone itself, the authors consider the annexed formula more probable than that advanced by Jerdan. When hydrolysed by hydrobromic acid it yields 4 : 5 : 7-trihydroxycoumarin. Acetylation of the lactone gives two products, one of which is a diacetyl derivative of acidic character whilst the other appears to be a di- or tri-acetyl lactone anhydride. Addition of alcohol to the lactone yields as by-products two anhydrides, the constitution of which has not been elucidated.



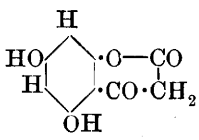
Phloracetophenone has been prepared in good yield by the action of water at 170° on Jerdan's lactone or ester and from the ester, $C_{17}H_{20}O_{10}$ (compare Meerwein, A., 1913, i, 858), and is identical with the monoacetyl*cyclo*hexantrione described by Heller (A., 1912, i, 274).

Acetylation of phloracetophenone-3-ω-dicarboxylic ester by acetic

anhydride and sodium acetate yields the acetyl derivative of the lactone, $C_{12}H_{10}O_7$, m. p. 197°, *ethyl diacetyl*-4 : 6-*dihydroxycoumarin*-β-*aceto*-3(5 ?)*carboxylate* [?], $C_{20}H_{20}O_{10}$, m. p. 142—143° and an uncrystallisable residue which is converted by hydrobromic acid (*D* 1·49) and glacial acetic acid into the acid $C_{11}H_8O_6$, m. p. 302°. The ester is oxidised by potassium permanganate to a *substance*, $C_{20}H_{20}O_{13}$, prisms, m. p. 169—170°, and is converted by hydrobromic acid into the acid $C_{11}H_8O_6$, which can also be obtained by hydrolysis of the non-crystalline product of acetylation. The acid is unchanged by prolonged boiling with saturated alcoholic hydrochloric acid, and with sodium acetate and acetic anhydride gives a *product*, $C_{15}H_{12}O_8$, needles, m. p. about 230° after previous slight decomposition, and small quantities of a *substance*, needles, m. p. 135°, which are insoluble in sodium hydroxide. When heated on the water-bath with aniline, the acid loses carbon dioxide and yields 5 : 7-dihydroxy-4-methylcoumarin, leaflets, m. p. about 277—279° (decomp.).

Ethyl phloracetophenone-3 : 5-dicarboxylate, m. p. 129°, is conveniently prepared by warming a solution of ethyl phloroglucinol-dicarboxylate in light petroleum with anhydrous ferric chloride and gradual addition of acetyl chloride. When acetylated with sodium acetate and acetic anhydride it gives an *acetyl* derivative, $C_{22}H_{22}O_{11}$, or $C_{20}H_{20}O_{10}$, m. p. 126—127°, which when hydrolysed with hydrobromic and glacial acetic acids yields a *product*, $C_{12}H_{10}O_5$, needles, m. p. 249—251° (*acetyl* derivative, $C_{16}H_{14}O_7$, thin prisms, m. p. 128—129°) which is not identical with dihydroxymethylcoumarin.

Jerdan's lactone is prepared by the action of sodium on a solution of acetonedicarboxylic ester in benzene. Contrary to the former statement, it does not give a coloration with concentrated or dilute nitric acid, even in the presence of sulphuric acid. As by-products, the following substances are described : *leaflets*, which decompose at about 285° and are difficultly soluble in acetic acid, *needles*, $C_{14}H_{14}O_7$, m. p. about 243° (decomp.), *prisms*, $C_{14}H_{16}O_8$, m. p. 192°.



Hydrolysis of the lactone by hydrobromic and acetic acids yields a substance, $C_9H_6O_5,2H_2O$ (annexed formula), needles, which, when rapidly heated, evolve gas at 180—190°, again solidify, and decompose above 210°. The anhydrous substance sinters and decomposes from 210° and is completely molten at 240—250°. When acetylated in the usual manner, the lactone gives a *substance*, $C_{18}H_{16}O_{10}$, or $C_{16}H_{14}O_9$, colourless needles, which soften at 185°, and have m. p. 196—197°, an *anhydride* of the di- or tri-acetyl lactone, yellow needles, m. p. about 237°, and a third *substance*, m. p. 197°, which could not be obtained in the pure condition. Hydrolysis of the di-acetyl derivative leads to the formation of a *substance*, $C_9H_6O_5$, and of a fluorescent *acid*, $C_{12}H_8O_8$, leaflets, which become red from 240° and have m. p. 260° (decomp.). Hydrolysis of the anhydride by hydriodic and glacial acetic acids gives a *product*, $C_{17}H_{14}O_9$ (?), almost colourless needles, which do not melt below 360°.

Treatment of Jerdan's lactone with boiling 5 per cent. alcoholic hydrogen chloride gives the ester, m. p. 92—93°, a crystalline *by-product*

$C_{14}H_{14}O_7$, m. p. 175—176°, which is regarded as an anhydride of phloracetophenonedicarboxylic ester and an amorphous residue which is converted by acetic anhydride and sodium acetate into an *acetyl* derivative, $C_{18}H_{18}O_9$, or $C_{20}H_{20}O_{10}$, leaflets, m. p. 154—155°. Acetylation converts the anhydride mentioned above into a *derivative*,

$$C_{18}H_{18}O_9 \text{ or } C_{20}H_{20}O_{10},$$

rhombs or plates, m. p. 161—162°. Both the anhydride and its acetyl derivative are converted by hydrolysis into the acid $C_9H_6O_5$.

Phloracetophenone, $C_8H_8O_4,H_2O$, needles, m. p. 218°, after softening at 200°, is obtained in 80 per cent. yield by heating Jerdan's ester or lactone or the ester $C_{17}H_{20}O_{10}$ with the double quantity of water at 160—170°. The properties of this substance agree generally with those of monoacetyl*cyclo*hexantrione described by Heller (*loc. cit.*), who, however, gives m. p. 209—210°, but differ from phloracetophenone obtained by Bülow and Wagner (A., 1901, i, 559) which was not molten at 280°. H. W.

The Beckmann Rearrangement. IV. Acyl Derivatives of the Substituted Imino-acids. Mitsuru Kuhara and Kanoichiro Suitsu (*Mem. Coll. Sci. Kyōtō*, 1914, **1**, 25—34; compare A., 1914, i, 538).—In his studies on the mechanism of the Beckmann rearrangement, Kuhara has made it seem probable that the acyl derivatives of the substituted imino-acids are formed as intermediate products. Attempts have therefore been made to synthesise such esters and to isolate them from the products of the Beckmann rearrangement of the ketoximes.

The first of these compounds to be prepared was phenylbenzimino-acetate, the hydrochloride of which (I) is regarded as an intermediary in the rearrangement of diphenylketoxime by acetyl chloride, thus :—

$$\underset{\text{N·OH}}{\overset{\text{CPh}_2}{\|}} \xrightarrow{\text{MeCOCl}} \underset{\text{HCl,N·OAc}}{\overset{\text{CPh}_2}{\|}} \longrightarrow \underset{\text{HCl,NPh}}{\overset{\text{CPh·OAc}}{\|}} \longrightarrow \underset{\text{NHPh}}{\overset{\text{PhCO}}{|}} + \text{MeCOCl}.$$

(I.)

The hydrochloride (I) is only stable in the cold, for it readily changes to benzanilide, and as diphenylketoxime acetate does not undergo rearrangement except under the influence of hydrochloric acid, the establishment of the hydrochloride as an intermediate product could not be proved. With a stronger acid residue the rearrangement is easier, and diphenylketoxime benzenesulphonate changes spontaneously into phenylbenzimino-benzenesulphonate (following abstract).

Success in the preparation of phenylbenzimino-acetate not being always assured, similar esters have been made for comparison. Perfectly pure phenylbenzimino-chloride and potassium thioacetate yield the thioacetate, SAc·CPh:NPh, but this is accompanied by acetylphenylthiobenzamide, S:CPh·NPhAc, if the chloride is not pure.

Silver acetate was gradually added to a cold, ethereal solution of phenylbenzimino-chloride and the resulting yellow solution was filtered and evaporated. Benzanilide, followed by acetylbenzanilide, crystallised out, leaving *phenylbenziminoacetate* as a thick, yellow oil which is

stable in solution even at 160—170°. Hydrogen chloride precipitates the *hydrochloride* (I) from a cold solution, as a canary-yellow powder which decomposes in moist air or at 60°. Sodium acetate and phenylbenzimino-chloride yielded acetylbenzanilide only, and silver benzoate produced benzanilide, benzoic acid, dibenzoylanilide, and some yellow oil.

Potassium thioacetate was slowly added to a solution of phenylbenzimino-chloride in light petroleum, mixed with anhydrous potassium carbonate. After a few days, a mixture of yellow phenylbenziminothioacetate with orange-red acetylphenylbenzamide separated. This was extracted with warm petroleum, which removed the orange crystals. *Phenylbenzimino-thioacetate* forms amber-yellow, monoclinic crystals, and is transformed into the isomeric *acetylphenylbenzamide*, m. p. 78·5—79·5°, by acyl chlorides, alkali hydroxides, or acid fumes. Both are converted into thiobenzanilide on warming with acids or alkalis, the former the more readily. Acetyl chloride produces the orange-red compound when added to a dry ethereal solution of thiobenzanilide, but yields a considerable amount of the yellow isomeride when added to a suspension of the sodium derivative of thiobenzanilide in xylene.

Potassium thiobenzoate yielded two similar compounds, *phenylbenzimino-thiobenzoate*, $C_6H_5\cdot CO\cdot S\cdot CPh{:}NPh$, yellow, and *benzoylphenylthiobenzamide*, $C_6H_5\cdot CS\cdot NPhBz$, orange-red, m. p. 110—111°.

J. C. W.

The Beckmann Rearrangement. V. Rearrangement of Diphenylketoxime Benzenesulphonate and Synthesis of Phenylbenziminobenzenesulphonate. Mitsuru Kuhara, Kaoru Matsumiya, and Naohiko Matsunami (*Mem. Coll. Sci. Kyōtō*, 1914, **1**, 106—113).—Diphenylketoxime benzenesulphonate changes spontaneously into a yellow, viscid liquid, in the solid state, in solution, or under the influence of ultra-violet rays. This liquid is phenylbenzimino-benzenesulphonate, which may be synthesised from pure phenylbenzimino-chloride and silver benzenesulphonate. The two products show the same absorption spectra and are decomposed readily by water into benzanilide and benzenesulphonic acid, or even benzoic acid, benzenesulphonic acid, and aniline. The assumption that the formation of an ester of the substituted imino-acid from the ketoxime ester plays a fundamental part in the Beckmann transformation is therefore definitely established.

The sodium salt of diphenylketoxime was prepared as a white powder by adding slices of the metal to an ethereal solution of the oxime, a small quantity of aminodiphenylmethane, $CHPh_2\cdot NH_2$, also being formed. The salt was shaken with benzenesulphonyl chloride and ether for some hours, when the filtrate deposited *diphenylketoxime benzenesulphonate*, $CPh_2{:}N\cdot O\cdot SO_2Ph$, in colourless crystals, m. p. 62°, which changed with explosive violence into the isomeride when heated above the m. p., and this, namely, *phenylbenzimino-benzenesulphonate*, $C_6H_5\cdot SO_2\cdot O\cdot CPh{:}NHPh$, prepared by any of the ways indicated above, deposited aniline benzenesulphonate when left in moist chloroform.

J. C. W.

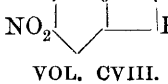
Preparation of Esters of Bicyclic β-Diketone-tetracarboxylic Acids. H. MEERWEIN (D.R.-P., 277,467; from *J. Soc. Chem. Ind.*, 1915, **34**, 249).—Mixtures of the esters of methylene-mono- or -di-malonic acids, or substances capable of yielding such mixtures, are treated with alkaline condensing agents. For example, the mixture of methyl methylenemalonate, methyl methylenedimalonate, and methyl *n*-pentane-$\alpha\alpha\beta\beta\delta\delta$-hexacarboxylate, obtained by the action of formaldehyde on methyl malonate, is treated with sodium methoxide, with the formation of methyl *bicyclo*[1 : 3 : 3]-nonane-2 : 6-dione-1 : 3 : 5 : 7-tetracarboxylate. *bicyclo*-Nonanedione and two isomeric dicarboxylates may be prepared from this. J. C. W.

Acetyl Derivatives of *s-m*-Xylenol. K. VON AUWERS (*Ber.*, 1915, **48**, 90—93).—The condensation of *s-m*-xylenol methyl ether with acetyl chloride in the presence of aluminium chloride gives rise to a ketone in which the carbonyl group is attached at the ortho-position to the hydroxyl of the original phenol. If the hydroxyl group of the xylenol is acetylated before the Friedel-Crafts reaction, the ketonic group attaches itself again in the same position, the para isomeride being absent from the product. A similar result is obtained if the phenolic acetate and acetyl chloride are made to react in the presence of zinc chloride, except that in this case the reaction is far from complete. This peculiar exclusive formation of the ortho-isomeride is still more remarkable in the fact that if a second acetyl radicle attaches itself to the ring during the Friedel-Crafts condensation, it enters at the remaining ortho-position.

5-*Methoxy*-m-*xylyl* 2-*methyl ketone*, $C_6H_2AcMe_2{\cdot}OMe$, forms colourless needles, m. p. 48—49°, b. p. 135°/14 mm.

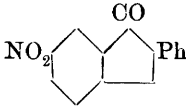
5-*Hydroxy*-m-*xylyl* 2-*methyl ketone* was obtained by direct condensation of the xylenyl acetate with acetyl chloride in the presence of aluminium chloride; it forms colourless needles, m. p. 57—58°, b. p. 140—141°/18 mm., 2 : 6-*Diacetyl*-m-5-*xylenol*, $C_6HAc_2Me_2{\cdot}OH$, obtained as a by-product in the preparation of the last substance, forms colourless needles, m. p. 109—110°. D. F. T.

Constitution of Phenyl-*m*-nitroindone. M. BAKUNIN and T. ANGRISANI (*Gazzetta*, 1915, **45**, i, 160—164).—Phenyl-*m*-nitroindone, prepared from phosphoric oxide and phenyl-*m*-nitrocinnamic acid, has been subjected, in chloroform solution, to the action of oxygen ozonised to the extent of 7%. The products comprise: (1) benzoic acid; (2) *4-nitro-2-aldehydobenzoic acid*, $CHO{\cdot}C_6H_3(NO_2){\cdot}CO_2H$, which forms crystals, m. p. 133—134°, and yields 4-nitrophthalic acid when oxidised with permanganate; (3) small proportions of *compounds*, m. p. above 300°, about 214° and about 180° respectively, which probably include the ozonide, $NO_2{\cdot}C_6H_3{\cdot}CH(O_3){\cdot}C(Ph)(CO)$, and the perozonide. The formation of benzoic and 4-nitro-2-aldehydobenzoic acids in this reaction indicates that phenyl-*m*-nitroindone has the structure (annexed formula).



T. H. P.

Constitution of Phenyl-*p*-nitroindone. M. BAKUNIN and A. KOSSINOVA (*Gazzetta*, 1915, **45**, i, 164—167).—The action of ozonised oxygen on phenyl-*p*-nitroindone, in suspension in chloroform, yields: (1) benzoic acid; (2) 5-nitro-2-aldehydobenzoic acid; (3) *p*-nitrobenzoic acid; (4) *p*-nitrobenzaldehyde and (5) a syrupy ozonide (?). The constitution of phenyl-*p*-nitroindone is, therefore, 6-nitro-2-phenylindone (annexed formula).



T. H. P.

Formation of Monophenolic Ketones and a New Synthesis of Benzotetronic Acid [4-Hydroxycoumarin]. H. PAULY and K. LOCKEMANN (*Ber.*, 1915, **48**, 22—32).—Contrary to the observation of Nencki (A., 1882, 1201), phenol readily undergoes condensation with acetic acid in the presence of zinc chloride, the expected *o*- and *p*-hydroxyacetophenones being separable without difficulty, in respective yields of approximately 5 and 11% of the theoretical. In contrast to the belief of Witt and Braun concerning the formation of the corresponding hydroxynaphthyl methyl ketones (*Ber.*, 1914, **47**, 3216), the authors do not regard the acetylation of the hydroxyl group as a necessary intermediate stage in the action. It is found that the additional presence of acetic anhydride has a less favourable effect in the acetylation of phenol than of naphthol, whereas an addition of acetyl chloride causes a marked increase in the yield of the *p*-acetyl derivative. The development of a yellow coloration during acetylation with or without the presence of acetyl chloride is regarded as indicative of the formation of an intermediate compound of organometallic type such as is assumed in the Friedel-Crafts reaction.

4-Hydroxycoumarin (benzotetronic acid) can be obtained in a yield 55% of the theoretical, by treating methyl *o*-acetoxybenzoate with sodium at 165—175°, condensation occurring according to the representation $C_6H_4<^{CO_2Me}_{OAc} \longrightarrow C_6H_4<^{C(OH):CH}_{O\text{---}CO}$. This condensation appears to be a general one for esters of *o*-acyloxybenzoic acids, and *methyl o-phenylacetoxybenzoate*, m. p. near 50°, b. p. 166—168°/2 mm., obtained by heating together methyl salicylate, phenylacetic acid, acetic anhydride, and a little sulphuric acid, likewise undergoes condensation on treatment with sodium at 160—165°, giving *phenylbenzotetronic acid* (*4-hydroxy-3-phenylcoumarin*), m. p. 236°.

D. F. T.

Formula of α-Santolinenone. L. FRANCESCONI and N. GRANATA (*Gazzetta*, 1915, **45**, i, 167—181).—The action of dilute acids on α-santolinenonehydroxylamino-oxime (compare A., 1914, i, 1202) has been studied. With the hydroxylamino-oximes of most hydrocyclic ketones, the action of a dilute acid consists in the elimination of the hydroxylamine joined to the double linking and subsequent hydrolysis of the oxime thus formed to the ketone. With α-santolinenone-hydroxylamino-oxime, however, this action proceeds quite differently

and is analogous to that occurring with pulegonehydroxylamine. Gradual decomposition takes place, yielding an oily imine:

$$CHPr^{\beta}\begin{<}CH_2\cdot C(N\cdot OH)\\ CH_2\text{---}CH_2\end{>}CH\cdot CH_2\cdot NH\cdot OH \longrightarrow$$

$$CHPr^{\beta}\begin{<}CH_2\cdot C(N\cdot OH)\\ CH_2\text{---}CH_2\end{>}C\begin{<}CH_2\\ NH\end{<} \longrightarrow CHPr^{\beta}\begin{<}CH_2\text{---}CO\\ CH_2\cdot CH_2\end{>}C\begin{<}CH_2\\ NH\end{<}.$$

When the imino-oxime is treated further with acid, the nucleus to which the oximic group is attached is opened and a molecule of water eliminated, with formation of an anhydrohydroxylamino-oxime, which exhibits extraordinary reducing power and is most probably a nitrile-imine of the structure, $CH_2{:}CPr^{\beta}\cdot CH_2\cdot CH_2\cdot C(C{:}N)\begin{<}CH_2\\ NH\end{<}$. Comparison of the properties of these different products with those of the corresponding ones obtained from pulegone confirms the structure previously assigned to α-santolinenone (*loc. cit.*).

α-Santolinenonehydroxylamino-oxime, $C_{10}H_{20}O_2N_2$, forms transparent, colourless, hexagonal prisms, m. p. 190°, at which temperature bubbles of gas are evolved and partial crystallisation occurs, fusion subsequently taking place at about 260° (compare Francesconi and Scarafia, A., 1911, i, 1001); simultaneous oxidation and reduction are effected when the hydroxylamino-oxime is fused, the products being an amino-oxime and a dioxime (*vide infra*). α-Santolinenonehydroxylamino-oxime forms an *oxalate*, m. p. 222° (decomp.) and a *dibenzoyl* derivative, $C_{24}H_{28}O_4N_2 + \frac{1}{2}H_2O$, m. p. 127—129° or, when anhydrous, 134°.

α-Santolinenoneamino-oxime, $NH_2\cdot C_{10}H_{17}{:}N\cdot OH$, obtained on heating the hydroxylamino-oxime, forms large crystals, m. p. 155°, and yields a hydrochloride, m. p. 246° (decomp.), for which the analytical results are intermediate to those of a mono- and a di-hydrochloride (compare Francesconi and Scarafia, *loc. cit.*).

α-Santolinenonedioxime, $C_{10}H_{16}(N\cdot OH)_2$, m. p. 260°, obtained by heating the hydroxylamino-oxime, or by treating it with mercuric oxide, is identical with that formed by the action of nitrous acid (*ibid.*); its dibenzoyl derivative has m. p. 157—158°.

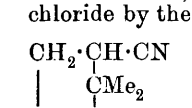
α-Santolinenoneanhydrohydroxylamino-oxime or *α-santolinenonenitrile imine*, $C_{10}H_{16}N_2$, forms prismatic crystals, m. p. 119—120°, and instantly reduces Fehling's solution, ammoniacal silver nitrate, or mercuric oxide solution in the cold. With sodium phosphomolybdate it gives a green and shortly afterwards a blue coloration, which is obtained immediately in presence of a little ammonia.

α-Santolinenoneimino-oxime, $C_{10}H_{18}ON_2$, forms small granules or cruciform crystals, m. p. 169—172°, and reduces Fehling's solution with difficulty in the hot, but readily even in the cold if previously treated with hydrochloric acid.

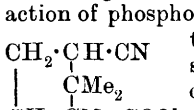
α-Santolinenone-imine, $O{:}C_{10}H_{16}{:}NH$, is obtained as a yellow oil exhibiting in aqueous solution the characteristic odour of nicotine bases. Gentle heating of the cold, saturated aqueous solution, even by the hand, causes the liquid to become milky, the imine separating in colourless, oily drops, having a density almost equal to that of the

solution; as the latter cools, the turbidity disappears, and the drops gradually redissolve. It reduces silver nitrate, mercuric oxide, or, with difficulty, Fehling's solution in the hot and exhibits many of the reactions of the alkaloids. Similar properties are shown by the base formed by the action of acids on pulegone-hydroxylamine (compare Semmler, A., 1904, i, 437). T. H. P.

Conversion of Oximinocamphor into Cyanolauronyl Chloride and Camphoceenonitrile. W. Borsche and W. Sander (*Ber.*, 1915, **48**, 117—120).—Attempts have been made to prepare cyanolauronyl chloride by the action of phosphorus pentachloride on oximinocamphor; the results are only partly successful, since a portion of the product immediately passes by loss of carbonic oxide and hydrogen chloride into camphoceenonitrile (Formula I.). The bulk of the latter is readily removed from the accompanying chloride (Formula II.) by fractional distillation, but the last traces cling so obstinately that, in order to prepare the pure chloride, it is necessary first to isolate the acid, and then to act on this with thionyl chloride.



(I.)



(II.)

A solution of oximinocamphor in dry ether is treated with phosphorus pentachloride. When the initial, vigorous action has subsided, the product is distilled, whereby two fractions are obtained, the first, b. p. 80—90°/15 mm., consisting of camphoceenonitrile, whilst the second, b. p. 150—180°/15 mm., is crude cyanolauronyl chloride. Repeated fractionation of the latter does not yield an analytically pure product, but its identity is established by converting it into cyanolauronoanilide, colourless needles, m. p. 198° (compare Haller and Minguin, A., 1896, i, 695). Cyanolauronyl chloride, b. p. 153—155°/15 mm., m. p. 99°, is obtained by the action of thionyl chloride in benzene solution on cyanolauronic acid, m. p. 150—151°, which is itself prepared by the action of dilute sodium hydroxide solution on the crude chloride, small quantities of cyanolauronic anhydride, m. p. 178°, being simultaneously formed.

Camphoceenonitrile has b. p. 90°/15 mm. It is reduced by hydrogen in the presence of colloidal palladium to *camphoceanonitrile*, $C_9H_{15}N$, m. p. 28—30°. Treatment with 5*N*-hydrochloric acid at 180° converts the latter into camphoceanic acid, $C_9H_{16}O_2$, colourless oil, b. p. 136—138°/15 mm. (compare Semmler, A., 1906, i, 682). H. W.

The Bile Pigments. VI. Mesobilirubin and Mesobilirubinogen. Hans Fischer. (*Zeitsch. Biol.*, 1914, **65**, 163—182).—A more complete account of recent investigations into the relationships between the degradation products of bilirubin (compare A., 1914, i, 1135).

Mesobilirubinogen (late hemibilirubin) is most readily converted into mesobilirubin by heating with a 10% solution of potassium methoxide at 150°. At 170°, however, xanthobilirubic acid is also formed. The two substances are easily separated, for mesobilirubin is soluble in chloroform and insoluble in hot, glacial acetic acid, whereas

xanthobilirubic acid is sparingly soluble in the former and readily so in the latter. A better yield of xanthobilirubic acid is obtained if the temperature is still further raised to 190°. The new specimens have m. p. 294°, whereas an earlier preparation had m. p. 274°, and another product obtained in the old way, by the action of sodium methoxide on bilirubic acid, had m. p. 285°. The methyl ester of the acid derived from mesobilirubinogen has m. p. 190°, whereas the ester of the acid obtained from bilirubic acid has m. p. 212° (*ibid.*). Both acids give identically the same bilirubic acid on reduction with sodium amalgam. The author does not doubt that, with more material, the identity of these xanthobilirubic acids will be more satisfactorily established.

Unsuccessful attempts were made to convert mesobilirubin into mesobilirubinogen by biological methods, but this transformation is easily effected by sodium amalgam.

The oxidation of mesobilirubin to methylethylmaleimide is carried out by slowly adding solid sodium nitrite to a suspension of the substance in glacial acetic acid, whereby the play of colours associated with Gmelin's reaction is strikingly manifested.

Bilirubin is also attacked by potassium methoxide at 100°, but the author could not isolate pure mesobilirubin from the product of the reaction. This reduction is best performed on an alkaline solution by means of colloidal palladium and hydrogen. On shaking the crude product with cold chloroform, there remained, in the new experiments, an insoluble part (A) which crystallised in brownish-red prisms, m. p. 320° (decomp.), from hot chloroform. This residue is neither bilirubin nor mesobilirubin, for the carbon content is low. In this respect it is analogous to the compound II. (A., 1911, i, 1005).

A substance, m. p. 87°, was recently obtained (A., 1914, i, 862) by the action of sodium nitrite and acetic acid on bilirubin. It has since been found that this changes completely in a few days, forming insoluble prisms, decomp. 260°, and that it contains nitrogen.

The isolation of mesobilirubinogen from pathological urine has been repeated, because the earlier method (A., 1911, i, 1004) yielded only a fraction of the "urobilinogens" present. As often as the daily urine responded to Ehrlich's aldehyde test, which was not every day, it was at once extracted with chloroform. The combined extracts from 40 litres yielded 0·02 gram of mesobilirubinogen, which was completely identified by crystallographic measurements, m. p., and reactions. No other substances which give the Ehrlich reaction were isolated and mesobilirubinogen is probably the only "urobilinogen."

It was observed that methylethylmaleimide crystallises in two forms. These will be described elsewhere, by Steinmetz.

J. C. W.

The Colouring Principle Myrica Rubra. Its Azo-, Sulphide, and Nitro-dyes. Sadakichi Satow (*J. Ind. Eng. Chem.*, 1915, **7**, 113—115).—The colouring matter obtained from the bark of *Myrica rubra* has the formula $C_{15}H_{10}O_8$; it contains 6 hydroxyl groups and in some of its properties it is identical with myricetin (compare A. G. Perkin, T., 1896, **69**, 1287; 1902, **81**, 203; 1911, **100**, 1721). It

dyes brownish-yellow, orange-yellow, orange-brown, and black, with alumina, tin, chrome, and iron mordants respectively. When myricetin is melted with sodium polysulphide and free sulphur, a substance is obtained which dyes cotton directly to a deep sepia colour; the addition of copper sulphate, manganese sulphate, or ferrous sulphate to the polysulphide mixture produces substances having a bluish-brown or bluish-grey colour. By melting myricetin with sulphur alone, a brown-yellow substance is obtained. A yellow dye may be prepared by nitrating myricetinsulphonic acid. W. P. S.

Tanning Power of Triacetin. Pietro Falciola (*Ann. Chim. Applicata*, 1915, i, 32—36).—Experiments made with calf-, lamb- and sheep-skins, show that emulsions, or aqueous or aqueous-alcoholic solutions, of triacetin exhibit marked tanning properties and may be employed with economic advantage. T. H. P.

Metal Additions in Liquid Ammonia. H. Schlubach (*Ber.*, 1915, **48**, 12—14).—The additive reaction between unsaturated compounds and the alkali metals generally occurs slowly (Schlenk and others, A., 1914, i, 396, 823), but it is now found to be very rapid when the solution of the unsaturated compound (preferably in ether) is treated with a solution of the alkali metal in liquid ammonia; an atmosphere of nitrogen is necessary. By using an excess of the unsaturated compound the isolation of the additive product is facilitated.

In the case of the red additive compound, *potassium dimethylpyrone*, the composition was proved by analysis; with benzophenone, stilbene, and naphthalene, the nature of the additive product was determined by subsequent decomposition with water; no additive reaction was observed with benzene at lower temperatures, whilst at higher temperatures the formation of sodamide interfered with the observations.

From these results it would appear that the reduction of aromatic hydrocarbons such as naphthalene by means of a solution of sodium in liquid ammonia (Lebeau and Picon, A., 1914, i, 825, 946) is to be referred to the hydrolytic decomposition of a primary additive compound, the reduction being possibly extended by the subsequent development of hydrogen on the addition of water to the sodammonium solution.

Organic halogen compounds of the ammonium and diazonium salt types are also found to react immediately with a solution of an alkali metal in liquid ammonia with formation of coloured products. D. F. T.

Addition of Auxochromes in the Flavone Group. Arthur George Perkin and Edwin Roy Watson (T., 1915, **107**, 198—209).—With the object of deepening the colour of the dye and of preparing new polyhydroxyflavones, Watson (T., 1914, **105**, 338) has endeavoured to introduce an additional hydroxyl group into the quercetin molecule, but without success, as it was found impossible to convert aminoquercetin pentamethyl ether, by means of the diazo-compound, into the corresponding hydroxy-derivative. The work has now been extended to luteolin and morin.

Luteolin was converted into the tetraethyl ether from which, however, only a tetranitro-derivative could be obtained under the most varied conditions of nitration. The introduction of a single nitro-group was effected by nitration of *monobromoluteolin tetraethyl ether* and the compound so obtained gave, on reduction, an *amino*-derivative which when diazotised and boiled with water, yielded *bromo-6′-hydroxyluteolin tetraethyl ether*. De-ethylation of this substance proved difficult, but the ultimate product closely resembled luteolin, no deepening of shade having occurred as the result of the introduction of the new hydroxyl group.

Morin pentamethyl ether gave, on nitration, *nitromorin pentamethyl ether*, which was reduced to the corresponding amino-derivative. Attempts to replace the amino-group by hydroxyl have hitherto failed. *Aminomorin hydriodide* dissolved in alkalis with a yellowish-brown tint, the additional auxochrome not having caused any noteworthy deepening of colour.

Spectroscopic examination shows that a multiplication of auxochromes seems to widen the principal absorption band and shift it a little towards the red end of ths spectrum, but whereas a slight broadening or shift of a band in the red, yellow, or green part of the spectrum has a great effect on the colour of the substance, the broadening or shifting to an equal extent of a band in the violet, extending from the ultra-violet into the violet end of the spectrum, has very little effect on the visible colour.

Derivatives of Luteolin. Tetranitrolutein tetraethyl ether, $C_{15}H_2O_2(OEt)_4(NO_2)_4$, colourless prisms, m. p. 196°. *Bromoluteolin tetraethyl ether perbromide*, $C_{15}H_2O_2(OEt)_4Br,HBr_3$, slender prisms, m. p. 161° (decomp.) after softening at 157°. *Bromoluteolin tetraethyl ether hydrobromide*, $C_{15}H_2O_2(OEt)_4Br,HBr,C_2H_4O_2$, hair-like needles, is converted by boiling water into bromoluteolin tetraethyl ether, colourless hexagonal plates, m. p. 183°. This substance is the main product of the action of water, alcohol and water, or dilute sulphuric acid on the perbromide described above and may be prepared by brominating luteolin tetraethyl ether in acetic acid solution and in the presence of sodium acetate. Under the latter circumstances, *tetrabromoluteolin tetraethyl ether*, $C_{15}H_2O_2Br_4(OEt)_4,H_2O$, colourless crystals, m. p. 111—114°, is also produced.

Bromo-6′-nitroluteolin tetraethyl ether, $NO_2{\cdot}C_{15}H_4O_2Br(OEt)_4$, forms cream-coloured rhombs, m. p. 170—171°. When reduced by stannous chloride and concentrated hydrochloric acid in alcoholic solution, it gives *bromo-6′-aminoluteolin tetraethyl ether*, yellow prisms, m. p. 165—169° [*hydrochloride*, $C_{15}H_4O_2Br(OEt)_4{\cdot}NH_2,HCl,H_2O$, bright yellow needles which become scarlet when dried over soda-lime, m. p. 187° (decomp.), *stannichloride*, $(C_{23}H_{26}O_6NBr)_4,H_4SnCl_6$, crimson prisms]. Reduction of bromonitroluteolin tetraethyl ether by alcoholic sodium sulphide gives a *substance*, needles, m. p. 187°, which has not yet been further investigated.

Bromo-6′-aminoluteolin tetraethyl ether yields a corresponding *diazonium chloride*, needles, which is transformed by boiling water into

bromo-6′-hydroxyluteolin tetraethyl ether, yellow needles, m. p. 255°. Its acetyl derivative forms white needles, m. p. 270—272°.

When bromohydroxyluteolin tetraethyl ether or its acetyl derivative is digested with boiling hydriodic acid (D 1·7), no solution apparently occurs, and the product appears to be *bromo-6′-hydroxyluteolin diethyl ether*, since, on acetylation, *bromo-6′-hydroxyluteolin diethyl ether triacetate*, m. p. 213°, is obtained. If acetic anhydride is added to the hydriodic acid, the product of the reaction yields, on acetylation, an acetyl derivative, white needles, m. p. 250—256°, after sintering at 225°, analyses of which agree approximately with the figures required by the formula $C_{15}H_5O_2(OAc)_5$. It is probable that the original substance is hydroxyacetyl-luteolin contaminated with a small amount of impurity. On hydrolysis, the acetyl derivative yields the free hydroxy-compound, which greatly resembles luteolin.

Nitro-3 : 4-diethoxybenzoic acid, colourless needles, m. p. 145—148°, is obtained by the oxidation of bromo-6′-nitroluteolin tetraethyl ether with potassium permanganate in alkaline solution.

Derivatives of Morin.—Morin pentamethyl ether is prepared either by Watson's process (*loc. cit.*) or by the action of methyl sulphate in alkaline solution (compare Herzig and Hofmann, A., 1909, i, 165). *Nitromorin pentamethyl ether*, $C_{15}H_4O_2(OMe)_5{\cdot}NO_2$, forms reddish-brown needles, m. p. 223—225°. *Amino-morin pentamethyl ether* forms colourless, hexagonal plates, m. p. 204—205°. It yields a *platinichloride*, stout yellow prisms. A definite compound could not be isolated from the product of diazotisation.

When morin pentamethyl ether is brominated in acetic acid solution, a substance is obtained which is brick-red at first and gradually assumes a pale colour; it is possibly the *dibromomorinpentamethyl ether perbromide*, which then slowly loses bromine with the formation of *dibromomorin pentamethyl ether hydrobromide*. Digestion with boiling sodium hydrogen sulphite solution converts it into *dibromomorin pentamethyl ether*, m. p. 263—270°. By the use of one molecular proportion of bromine, a *compound*, m. p. 200—205°, probably bromomorin pentamethyl ether, can be isolated, investigation of which has not been completed. Attempts to nitrate dibromomorin pentamethyl ether gave unsuccessful results.

Aminomorin hydriodide, $C_{15}H_4O_2(OH)_5{\cdot}NH_2,HI,H_2O$, is obtained by digesting nitromorin pentamethyl ether with hydriodic acid (D 1·7). It crystallises in spherulites or square platelets. H. W.

Coumaranone and a New Cyclic System Containing Nitrogen and Oxygen. R. Stoermer and E. Barthelmes (*Ber.*, 1915, **48**, 62—70).—In an endeavour to prepare an alcohol corresponding with coumaran (compare Stoermer and König, A., 1906, i, 200) the authors have now made 4-methylcoumarone a starting point. This substance, m. p. 52°, they obtained by elimination of the elements of water from *p*-tolylacetic acid, or by the intramolecular condensation of *p-tolylacetyl chloride* (colourless needles, m. p. 23°, b. p. 135°/20 mm.) in carbon disulphide solution under the influence of aluminium chloride. The methylcoumarone was then converted into the oxime

and reduced in alcoholic solution by sodium amalgam and acetic acid to *3-amino-5-methylcoumaran*, $C_6H_3Me<^{O}_{CH(NH_2)}>CH_2$, a colourless, viscous oil, b. p. 112—115°/25 mm., which is a strong base forming a solid *carbonate*, a *hydrochloride* (needles, m. p. 230°, which on dry distillation gives methylcoumarone and ammonium chloride), and a *platinichloride* (yellowish-red crystals which begin to decompose at 225° but remain unfused at 300°); ethyl chlorocarbonate converts the base into *2-carbethoxyamino-4-methylcoumaran*, needles, m. p. 93°, whilst the action of phenylcarbimide gives *4-methylcoumaranyl phenyl carbamide*, needles, m. p. 250—251° (decomp.). Treatment of the hydrochloride with sodium nitrite solution in the cold causes the formation of the unstable *nitrite*, needles, m. p. 130° (decomp.), which under the action of hydrochloric acid loses nitrogen with production of *5-methylcoumaranyl nitrite*, $C_6H_3Me<^{O}_{CH(NO_2)}>CH_2$, colourless needles, m. p. 72°. It was, however, found impossible to obtain the corresponding alcohol from this, because of its tendency to decompose, giving 5-methylcoumarone and nitrous acid.

The behaviour of coumarone towards the Grignard reagent was then examined and it was found that although coumarone homologues (resulting from the primarily formed tertiary alcohols by rearrangement) could be obtained, the yields were poor, probably owing to the considerable enolisation of coumarone in ethereal solution. By this reaction with magnesium methyl iodide, magnesium ethyl bromide, and magnesium phenyl iodide respectively, 3-methylcoumarone, $C_6H_4<^{O}_{CMe}>CH$, b. p. 196—197°/742 mm., *3-ethylcoumarone*, a pale yellow liquid, b. p. 217—218°/742 mm., of persistent odour, and 3-phenylcoumarone were obtained, whilst starting with 5-methylcoumarone the corresponding products were 3 : 5-dimethylcoumarone, b. p. 221—222°/742 mm., *5-methyl-3-ethylcoumarone*, pale yellow liquid of persistent odour, b. p. 237—238°/742 mm., and *3-phenyl-5-methylcoumarone*, a sweet-smelling oil, b. p. 328—329°/742 mm.

When *o*-nitrobenzylidenecoumarone (Stoermer and Atenstädt, A., 1903, i, 41) is treated in boiling alcoholic solution with an aqueous solution of sodium hyposulphite, reduction is effected to the corresponding amino-derivative, which immediately undergoes intramolecular condensation to a compound of the structure

$$C_6H_4<^{CH:C\cdot O}_{N=C\cdot C_6H_4}.$$

his substance, m. p. 153—154°, forms a *hydrochloride*, yellow needles, . p. 245°, a *platinichloride*, red-yellow needles, not fused at 300°, and an *aurichloride*, gold yellow needles, not fused at 300°. From its analogy in structure to quindoline, $C_6H_4<^{CH:C\cdot NH}_{N=C\cdot C_6H_4}$, and thioquindoline, $C_6H_4<^{CH:C\cdot S}_{N=C\cdot C_6H_4}$, which it resembles in forming coloured salts, this substance is named *coumarinoline*. In a similar manner

5-methyl-o-nitrobenzylidenecoumaranone,

$$C_6H_3Me\langle\begin{matrix}-O-\\CO\end{matrix}\rangle C{:}CH\cdot C_6H_4\cdot NO_2,$$

orange-red needles, m. p. 154°, can be reduced to a *methylcoumarinoline*, needles, m. p. 149—150°; *hydrochloride*, yellow needles, m. p. 220°; *platinichloride*, reddish-yellow crystals unfused at 300°. D. F. T.

A Synthesis of Fisetin. K. von Auwers and P. Pohl (*Ber.*, 1915, **48**, 85—90).—Except by the method commencing with the monomethyl or ethyl ether of resorcinol (Kostanecki, Lampe, and Tambor, A., 1904, i, 441; Kostanecki and Nitkowski, A., 1905, i, 915), no other synthesis of fisetin has hitherto been effected. A scheme for another possible method has been indicated (Auwers and Müller, A., 1909, i, 145) passing successively through 6-methoxycoumaranone, *m-p*-dimethoxybenzylidene-6-methoxycoumaranone, the dichloride additive product of the last-named, fisetin trimethyl ether, and hence finally to fisetin itself,

$$OMe\cdot C_6H_3\langle\begin{matrix}-O-\\CO\end{matrix}\rangle CH_2 \longrightarrow OMe\cdot C_6H_3\langle\begin{matrix}-O-\\CO\end{matrix}\rangle C{:}CH\cdot C_6H_3(OMe)_2 \longrightarrow$$

$$OMe\cdot C_6H_3\langle\begin{matrix}-O-\\CO\end{matrix}\rangle CCl\cdot CHCl\cdot C_6H_3(OMe)_2$$

$$\longrightarrow \begin{matrix}C_6H_3(OMe)\cdot O\\ |\\ CO\text{—}C(OH)\end{matrix}\rangle C\cdot C_6H_3(OMe)_2 \longrightarrow \begin{matrix}C_6H_3(OH)\cdot O\\ |\\ CO\text{—}C(OH)\end{matrix}\rangle C\cdot C_6H_3(OH)_2$$

The mechanism of the type of change involved in the penultimate stage has recently been examined (A., 1914, i, 981) with the discovery that a substituent radicle in the para position to the oxygen atom of the coumaranone ring in such a compound, facilitates the formation of a flavonol derivative, whilst the substitution in the meta position favours elimination of hydrogen chloride with re-formation of the coumaran ring. The authors have therefore returned to the problem of the above synthesis, in the hope of finding a small quantity of the desired trimethoxy-compound in the reaction product.

m-p-Dimethoxybenzylidene-6-methoxycoumaranone was converted into the *dibromide* and *dichloride*. The former was insufficiently stable, but the latter, yellow crystals, m. p. 160—170°, when treated with a dilute alcoholic sodium hydroxide solution, yielded fisetin trimethyl ether to the extent of 5% of the theoretical amount. By heating the acetyl derivative of the ether with hydriodic acid, fisetin itself was obtained. D. F. T.

Synthesis of Gluco-*m*-hydroxycoumarin and Glucoprotocatechuic Acid. F. Mauthner (*J. pr. Chem.*, 1915, [ii], **91**, 174—179).—In view of the wide-spread occurrence of coumarin glucosides in plants, the author has undertaken the synthesis of these substances, the present paper dealing with the preparation of the glucoside of *m*-hydroxycoumarin.

Tetra-acetylgluco-m-*hydroxycoumarin*, prepared by the condensation of acetobromoglucose with *m*-hydroxycoumarin with sodium hydroxide in aqueous acetone solution at the ordinary temperature, crystallises in colourless needles, m. p. 177—178°, and is hydrolysed by aqueous

barium hydroxide to *gluco*-m-*hydroxycoumarin*, $C_{15}H_{16}O_8$, colourless needles, m. p. 219—220°, with previous sintering at 210°.

Methyl tetra-acetylglucoprotocatechuate, $C_{22}H_{27}O_{13}$, prepared from acetobromoglucose and methyl protocatechuate in a similar manner, form colourless needles, m. p. 167—168°, and on hydrolysis with aqueous barium hydroxide yields *glucoprotocatechuic acid*, $C_{13}H_{16}O_9$, which crystallises in very hygroscopic needles, softening at 70°, m. p. 81—82°, $[\alpha]_D^{17} - 75{\cdot}94°$ in aqueous solution, and gives a yellow coloration with ferric chloride. F. B.

The Thiophen Series. VI. Condensation of Thiophen with Phthalic Anhydride. Wilhelm Steinkopf (*Annalen*, 1914, **407**, 94—108. Compare A., 1914, i, 425, 426, 427, 432). [With W. Butkiewicz] —o-2-*Thienoylbenzoic acid*, $CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}C_4SH_3$, colourless crystals, m. p. 145°, is prepared from thiophen, phthalic anhydride, and aluminium chloride in carbon disulphide in the usual manner. Its constitution is proved by the formation of the compound by the oxidation of *o*-tolyl 2-thienyl ketone by chromic and acetic acids. The *ethyl* ester, m. p. 64°, b. p. 221·5—222°/13 mm., is prepared from the silver salt and ethyl iodide or from ethyl-alcoholic hydrogen chloride. The *ψ-ethyl* ester, $C_4SH_3{\cdot}C(OEt)\begin{matrix}O{\cdot}CO\\ \diagup\!\!\diagdown\\ C_6H_4\end{matrix}$, m. p. 69—70°, b. p. 210—212°/14 mm., is obtained from the thienoylbenzoyl chloride (prepared by means of thionyl chloride or phosphorus pentachloride; compare Meyer, A., 1908, i, 26) and ethyl alcohol or by heating the acid with acetic anhydride and subsequently with ethyl alcohol. The *ψ*-ester, but not the normal ester, reacts with alcoholic ammonia; the *ψ-amide*,

$$C_4SH_3{\cdot}C(OH)\begin{matrix}NH{\cdot}CO\\ \diagup\!\!\diagdown\\ C_6H_4\end{matrix}\ (?),$$

forms colourless, microscopic crystals, m. p. 137—138°.

o-Thienoylbenzoic acid reacts with hydroxylamine hydrochloride and aqueous potassium hydroxide to form an *anhydro-oxime*,

$$C_4SH_3{\cdot}C\begin{matrix}N{\cdot}O\\ \diagup\!\!\diagdown\\ C_6H_4\end{matrix}>CO,$$

faintly brown needles, m. p. 135—136°, and yields a *nitro*-derivative, $C_{12}H_7O_5NS$, m. p. 199—200°, yellowish-white crystals, by treatment with nitric acid, D 1·5.

Thiophanthraquinone, $C_6H_4\begin{matrix}CO\\ \diagup\!\!\diagdown\\ CO\end{matrix}>C_4SH_2$, yellow needles, m. p. 227—228°, prepared by heating *o*-thienoylbenzoic acid with phosphoric oxide at 150°, or with concentrated sulphuric acid at 105°, sublimes readily, forms a brownish-yellow vat with alkaline hyposulphite, and yields a *nitro*-derivative, $C_{12}H_5O_4NS$, yellow crystals, m. p. 240—241°, by treatment with nitric acid, D 1·5. C. S.

Thianthren. II. K. Fries and E. Engelbertz (*Annalen*, 1915, **407**, 194—228; compare Fries and Vogt, A., 1911, i, 555).—The formulation of thianthren dichloride as an ortho-quinonoid dithionium salt (*loc. cit.*) has hitherto not been supported by the isolation of salts other than the dichloride. Since, by analogy with other similar substances, the introduction of methyl, methoxy-, or amino-groups into the thianthren nucleus should increase the basic character of the

hypothetical dithionium hydroxide, the authors have examined 3 : 7-dimethoxy- and 3 : 7-dihydroxy-thianthrens in the hope of isolating stable quinonoid thianthrenthionium salts.

The authors failed to prepare the dimethoxy- and dihydroxythianthrens by the usual methods ; also, attempts to introduce the hydroxy-, nitro-, or sulpho group into thianthren by the customary processes were unsuccessful.

p-*Thioacetanisidide*, $OMe\cdot C_6H_4\cdot NH\cdot CS\cdot CH_3$, colourless leaflets, m. p. 118°, obtained by heating *p*-acetanisidide and phosphorus pentasulphide in boiling toluene, is oxidised by cold 2*N*-sodium hydroxide and potassium ferricyanide to 5-*methoxy*-1-*methylbenzothiazole*,

$$OMe\cdot C_6H_3\langle\begin{matrix}N\\S\end{matrix}\rangle CMe.$$

This substance is converted by alcoholic potassium hydroxide at 190—195° into 2-*amino*-5-*methoxyphenyl mercaptan*, the *diazosulphide* of which, $OMe\cdot C_6H_3\langle\begin{matrix}S\\N\end{matrix}\rangle N$, colourless needles, m. p. 72°, gives a poor yield of 3 : 7-dimethoxythianthren by heating at 200°. *Di*-2-*amino*-5-*methoxyphenyl disulphide*, slender needles, m. p. 82°, is obtained by the oxidation of the preceding mercaptan in the air.

3 : 7-*Dimethoxythianthren*, $OMe\cdot C_6H_3\langle\begin{matrix}S\\S\end{matrix}\rangle C_6H_3\cdot OMe$, leaflets, m. p. 133—134°, is readily prepared by treating *m*-methoxyphenyl mercaptan with concentrated sulphuric acid cooled by water. In glacial acetic acid it is oxidised, in hot solution, by dilute nitric acid to the *monosulphoxide*, $OMe\cdot C_6H_3\langle\begin{matrix}SO\\-S-\end{matrix}\rangle C_6H_3\cdot OMe$, colourless needles, m. p. 154—155°, and at the ordinary temperature by nitric acid (D 1·4) to the *disulphoxide*, $C_{14}H_{12}O_4S_2$, needles, m. p. 266—268°. 3 : 7-*Dimethoxythianthrendisulphone*, $C_{14}H_{12}O_6S_2$, colourless leaflets, m. p. 282°, prepared by oxidising dimethoxythianthren in boiling glacial acetic acid and hydrogen peroxide, is converted by boiling alcohol and 75% aqueous potassium hydroxide into 4′ : 5-*dimethoxy*-2′-*ethoxydiphenyl sulphone*-2-*sulphinic acid*, $SO_2H\cdot C_6H_3(OMe)\cdot SO_2\cdot C_6H_3(OMe)\cdot OEt$, colourless crystals, m p. 133°. The methods of preparation and the reactions of the preceding substances are similar to those of the corresponding thianthren derivatives (*loc. cit.*), but 3 : 7-dimethoxythianthrendisulphoxide has been obtained in only one form, and the sulphinic acid is converted by hydrogen bromide in boiling glacial acetic acid into 4-*bromo*-4′ : 5-*dimethoxy*-2′-*ethoxydiphenylsulphone disulphide*,

$$[OEt\cdot C_6H_3(OMe)\cdot SO_2\cdot C_6H_2Br(OMe)]_2S_2,$$

colourless crystals, m. p. 225°. The preceding reagent similarly converts the disulphoxide into ?:?-*dibromo*-3 : 7-*dimethoxythianthren*, $C_{14}H_{10}O_2Br_2S_2$, stout needles, m. p. 235°.

When 3 : 7-dimethoxythianthren is dissolved in concentrated sulphuric acid, sulphur dioxide is evolved and a deep blue solution formed. By the absorption of moisture from the atmosphere the solution deposits a hemiquinonoid 3 : 7-*dimethoxythianthrendithionium hydrogen sulphate*,

$$OMe\cdot C_6H_3\langle\begin{matrix}S(O\cdot SO_3H)\\S(O\cdot SO_3H)\end{matrix}\rangle C_6H_3\cdot OMe, OMe\cdot C_6H_3\langle\begin{matrix}S\\S\end{matrix}\rangle C_6H_3\cdot OMe,$$

bluish-black leaflets with a bronze lustre, m. p. 184—186° (decomp.). The sulphate forms blue solutions in concentrated sulphuric, hydrochloric, and formic acids, liberates iodine from aqueous potassium iodide, and oxidises stannous chloride, 3 : 7-dimethoxythianthren being regenerated in both cases. All these properties are consistent with those of a quinonoid thionium salt, but since 2 mols. of dimethoxythianthren are obtained for each atom of oxygen used in the preceding oxidations, the sulphate is formulated as a hemiquinonoid salt, as above. In agreement with this formula, the sulphate is hydrolysed by water, yielding 3 : 7-dimethoxythianthren and its sulphoxide. A para-quinonoid constitution of the sulphate is excluded because the salt does not yield methyl sulphate, even by heating.

There can be little doubt that a similar hemiquinonoid dithionium sulphate is formed when colourless thianthren dissolves in concentrated sulphuric acid, because, not only is sulphur dioxide evolved, but also the blue solution yields by hydrolysis with water thianthren and its sulphoxide; the formation of the latter was previously overlooked (*loc. cit.*). The analogy of the blue salts of thianthren to ditertiary dihydrophenazonium salts is now certainly established, because to these also the hemiquinonoid structure has been assigned (Kehrmann and Micewicz, A., 1912, i, 1020; Wieland, A., 1913, i, 1386).

In addition to the hemiquinonoid sulphate of 3 : 7-dimethoxythianthren, the corresponding *chloride*, $C_{14}H_{12}O_2Cl_2S_2$,$C_{14}H_{12}O_2S_2$, blue crystals with a bronze lustre, m. p. 104—105° (decomp.), and *ferrichloride*, $C_{28}H_{24}O_4Cl_2S_4$,$2FeCl_3$, dark blue crystals, have been prepared by the action of chlorine on dimethoxythianthren in cold benzene and of ferric chloride in boiling glacial acetic acid respectively. The hydrolysis of these salts by water is similar to that of the sulphate. The blue solutions obtained with 3 : 7-dimethoxythianthren and stannic chloride, antimony chloride, and perchloric acid are doubtless due to the formation of a hemiquinonoid stannichloride, antimonichloride, and perchlorate. Blue salts are formed even with hydrochloric acid, trichloroacetic acid, and aluminium chloride. In these cases atmospheric oxygen is doubtless the oxidising agent, because, when hydrogen chloride is passed into a solution of 3 : 7-dimethoxythianthren in glacial acetic acid a blue solution is or is not produced according as air is admitted or excluded. So great is the tendency of 3 : 7-dimethoxythianthren to form hemiquinonoid derivatives that holoquinonoid salts have not been obtained, the action of an excess of chlorine, of bromine, and of ferric chloride yielding colourless substitution products, a *perbromide* of the hemiquinonoid bromide, and the hemiquinonoid ferrichloride respectively. 3 : 7-Dimethoxythianthrenmonosulphoxide, unlike the corresponding thianthren derivative, does not yield holoquinonoid salts by treatment with hydrogen chloride and with concentrated sulphuric acid. In the former case the hemiquinonoid chloride is obtained, whilst in the latter the initially violet-red solution (which possibly contains the holoquinonoid sulphate) ultimately becomes blue and deposits the hemiquinonoid sulphate and, after the addition of water, 3 : 7-dimethoxythianthren and its sulphoxide. The same behaviour was previously observed with thianthrenmonosulphoxide (*loc. cit.*), but its significance was not appreciated.

3 : 7-*Dihydroxythianthren*, $C_{12}H_8O_2S_2$, colourless needles, m. p. 233°, is readily obtained by heating the dimethoxy-compound with hydrogen bromide in glacial acetic acid at 100°. The *monosulphoxide*, $C_{12}H_8O_3S_2$, prisms, m. p. above 300°, is obtained by the action of glacial acetic acid and hydrogen peroxide at the ordinary temperature. The behaviour of 3 : 7-dihydroxythianthren with concentrated sulphuric acid is quite similar to that of the dimethoxy-compound. The *dithionium hydrogen sulphate*,

$$OH\cdot C_6H_3\begin{matrix}S(O\cdot SO_3H)\\S(O\cdot SO_3H)\end{matrix}C_6H_3\cdot OH, OH\cdot C_6H_3\begin{matrix}S\\S\end{matrix}C_6H_3\cdot OH,$$

blue prisms, m. p. 198—202° (decomp.), *chloride*, $C_{24}H_{16}O_4Cl_2S_4$, m. p. 118° (decomp.), and *bromide*, $C_{24}H_{16}O_4Br_2S_4$, dark blue crystals, are stable in the dry state, and are reduced to 3 : 7-dihydroxythianthren by stannous chloride. It is noteworthy that whilst the sulphate of the dimethoxy-compound yields equal quantities of dimethoxythianthren and its sulphoxide by hydrolysis with water, the preceding sulphate yields an amorphous product which is not reduced to 3 : 7-dihydroxythianthren by stannous chloride and is only sparingly soluble in concentrated sulphuric acid, giving a bluish-green solution. Holoquinonoid derivatives of 3 : 7-dihydroxythianthren have not been obtained. C. S.

The Oxidation of Aconitine. George Barger and Ellen Field (T., 1915, **107**, 231—233).—The oxidation products of aconitine have been investigated by Carr (T., 1912, **101**, 2241), who obtained a substance termed oxonitin, to which the formula $C_{23}H_{29}O_9N$ was ascribed, and by Brady (T., 1913, **103**, 1821) who isolated a similar product, to which he gave the formula $C_{24}H_{29}O_9N$. The yields obtained by Brady were small, whilst, by Carr's process, the yields were greater but variable. The authors show that the loss in the older experiments was partly due to hydrolysis of aconitine permanganate by the sulphuric acid employed; when, however, aconitine is oxidised in acetone solution by means of potassium permanganate, glacial acetic acid being gradually added during the process, oxonitin, stout prisms, m. p. 276—277°, is obtained in 90 per cent. yield.

Analyses of oxonitin purified by different methods give figures which agree fairly closely with those obtained by Brady, but not with those of Carr. The agreement in m. p. and analysis of a specimen of oxonitin obtained by Carr's method lead the authors to the conclusion that the oxidation product is identical in whatever way the substance is prepared. A perfectly satisfactory formula has not yet been established.

When heated with fuming nitric acid, oxonitin yields the same oxidation product as aconitine itself, namely, the nitrosocarboxylic acid described by Brady.

Treatment of oxonitin with hydriodic acid (D 1·96) and red phosphorus at 285° leads to the formation of a substance, prisms, m. p. 121—122°, b. p. about 200°/15 mm., investigation of which is not yet complete. H. W.

Hydrogenation of Cinchonine. MARTIN FREUND and J. ANTON W. BREDENBERG (*Annalen*, 1914, **407**, 43—84).—According to the constitution at present accepted, the reduction of the cinchonine molecule may proceed in two regions, at the vinyl group and at the pyridine nucleus. The authors, employing Tafel's electrolytic method, confirm his observation that four atoms of hydrogen are utilised, but find, contrary to his experience, that the product can be separated into an oily *base* and a crystalline *base*, m. p. 134—135°, both of which have the formula $C_{19}H_{24}N_2$. The reduction is effected at a lead cathode in 50% sulphuric acid at 30—35°, using a divided cell and a cathode density of 0·023 amp./cm.^{2} at 24 volts.

The crystalline base, m. p. 134—135°, is converted, in the form of a salt, into deoxycinchonine by aqueous alcoholic iodine or boiling aqueous mercuric chloride, and is therefore *dihydrodeoxycinchonine* and contains very probably a partially reduced pyridine nucleus. It has an alkaline reaction to litmus and an intensely bitter taste, and in alcohol has $[\alpha]_D^{20}+250°$. It forms a *hydriodide*, $C_{19}H_{24}N_2,HI$, m. p. 197—198°, *dihydriodide*, $C_{19}H_{24}N_2,2HI$, m. p. 194—195°, *hydrobromide*, m. p. 205°, *oxalate*,, m. p. 125—126° (decomp.), *nitrate*, $C_{19}H_{24}N_2,2HNO_3,\frac{1}{2}H_2O$, m. p. 146—147°, *stannochloride*,

$$C_{19}H_{24}N_2,2SnCl_2,2HCl,H_2O,$$

m. p. 136—137°, *platinichloride*, decomp. 225°, an oily *nitroso*-derivative, an *acetyl* derivative (*hydriodide*, $C_{19}H_{23}N_2Ac,HI$, m. p. 240—241°; *platinichloride*, pale yellow needles, m. p. 205°), and a *benzoyl* derivative (*hydriodide*, $C_{19}H_{23}N_2Bz,HI$, colourless prisms, m. p. 250—251°).

By reduction with sodium and hot amyl alcohol, dihydrodeoxycinchonine is converted into *tetrahydrodeoxycinchonine*, a viscous, brown oil, which has $[\alpha]_D^{15}+64·6°$ in about 3% alcoholic solution, and forms a *hydriodide*, $C_{19}H_{26}N_2,HI$, m. p. 186—187°, *dihydriodide*, yellow needles, m. p. 274—275°, and *nitroso-hydrochloride*,

$$C_{19}H_{25}ON_3,HCl,$$

yellow needles, m. p. 195° (decomp.). With regard to its constitution, the following evidence indicates that the two additional hydrogen atoms in tetrahydrodeoxycinchonine have entered the partially reduced pyridine nucleus, not the vinyl group. By reduction in aqueous alcoholic solution with hydrogen and colloidal palladium, dihydrodeoxycinchonine is converted into a tetrahydrodeoxycinchonine isomeric with the preceding. Since cinchonine is attacked at the vinyl group and is converted into cinchotine by Paal's method of reduction, it is very probable that the tetrahydrodeoxycinchonine obtained by this method is *dihydrodeoxycinchotine*, whilst the isomeride produced by the sodium-amyl alcohol method still retains the vinyl group and is a tetrahydropyridine derivative.

Dihydrodeoxycinchotine, $C_{19}H_{26}N_2$, m. p. 72—73°, separates from ethyl ether in colourless crystals containing Et_2O, m. p. 61—62°. The base has $[\alpha]_D^{15}+324°$ in about 2% alcoholic solution, absorbs carbon dioxide, is alkaline to litmus, and instantly decolorises acidified potassium permanganate. It forms a *hydriodide*, $C_{19}H_{26}N_2,HI$, m. p. 225—226°, *dihydriodide*, m. p. 232—233° (decomp.), *perchlorate*, m. p. 234—235°, *acetyl* derivative [*hydriodide*, m. p. 245—246° (decomp.)],

nitroso-derivative [*hydrochloride*, $C_{19}H_{25}ON_3,HCl$, greenish-yellow needles, m. p. 195° (decomp.)], and *benzoyl* derivative (*hydriodide*, $C_{19}H_{25}N_2Bz,HI$, m. p. 225—226°; *dihydriodide*, m. p. 231—232°). By the action of methyl iodide in ethyl ether, the base yields *methyldihydrodeoxycinchotine hydriodide*, $C_{19}H_{25}N_2Me,HI$, colourless prisms, m. p. 183—184°, which is converted by alcoholic sodium methoxide and methyl iodide into *methyldihydrodeoxycinchotine methiodide*, $C_{19}H_{25}N_2Me,MeI$, greenish-white needles, m. p. 271—272° (decomp.).

The reduction of cinchotine by Tafel's method is quite analogous to that of cinchonine, dihydrodeoxycinchotine, identical with that described above, being obtained in about 50% yield; a second product of the reduction is another base which does not form a crystalline hydriodide. In contrast to the behaviour of dihydrodeoxycinchonine, dihydrodeoxycinchotine is not oxidised to deoxycinchotine by iodine or mercuric chloride.

In accordance with the expectation excited by the preceding reactions, the reduction of tetrahydrodeoxycinchonine by hydrogen and palladium and the reduction of dihydrodeoxycinchotine by sodium and amyl alcohol yield one and the same base *tetrahydrodeoxycinchotine* or *hexahydrodeoxycinchonine*, $C_{19}H_{28}N_2$, which forms a *hydriodide*, m. p. 225—226°, *dihydriodide*, m. p. 277—278°, and an oily *nitroso*-derivative.

The oily base, $C_{19}H_{24}N_2$, obtained by the electrolytic reduction of cinchonine (see above), has b. p. 295°/18 mm., and $[\alpha]_D^{20}+95{\cdot}8°$ in about 4% alcoholic solution, and forms a *platinichloride*,

$$C_{19}H_{24}N_2,H_2PtCl_6;$$

it has been named *isodihydrodeoxycinchonine*. C. S.

Preparation of Dihydromorphine. F. Hoffmann, La Roche & Co. (D.R.-P., 278,107; from *J. Soc. Chem. Ind.*, 1915, **34**, 249).—The crude product obtained by the catalytic reduction of neutral or acid, aqueous or aqueous alcoholic extracts of opium is acidified, if necessary, and evaporated to dryness, when the impurities are washed out by absolute alcohol, leaving the salt of dihydromorphine.

J. C. W.

Preparation of Alkyl Ethers and Acyl Derivatives of Dihydromorphine. Knoll & Co. (D.R.-P., 278,111; from *J. Soc. Chem. Ind.*, 1915, **34**, 249).—The base is treated with the appropriate agents in the usual manner. J. C. W.

Scission of Decahydroquinoline into its Optical Antipodes. II. L. Mascarelli and F. Nigrisoli (*Gazzetta*, 1915, **45**, i, 106—118; compare Mascarelli and Recusani, A., 1912, i, 761; Veneziani, A., 1913, i, 1228).—Decahydroquinoline, in which only the two central carbon atoms are asymmetric, may be readily obtained by the hydrogenation of quinoline under high pressure and in presence of colloidal platinum or palladium in an Ipatiev apparatus. Resolution of the synthetic compound into its optical antipodes, effected by treating the hydrochloride of the base with the calculated proportion of silver *d*-bromocamphorsulphonate, yielded: (1) *d*-Decahydroquinoline *d*-bromocamphorsulphonate, m. p. 239—240°, $[\alpha]_D^{25}$ +71·06° or, in

alcoholic solution, +72·88°. *d*-Decahydroquinoline forms long, white needles or prisms, showing slight contraction at 70°, m. p. 75—76°, b. p. 200—202°/760 mm., $[\alpha]_D^{25}$ in alcohol +4·81°; its hydrochloride, m. p. 303—304°, has very slight rotatory power in aqueous solution. (2) *l*-Decahydroquinoline *d*-bromocamphorsulphonate, softening at 171—172°, m. p. 175°, $[\alpha]_D^{25}$ +61·3°, or, in alcoholic solution, +74·2°. *l*-Decahydroquinoline forms a crystalline mass, softening at 70°, m. p. 74—75°, b. p. 200—201°/760 mm., $[\alpha]_D^{25}$ in alcohol −4·5°; its hydrochloride, m. p. 305°, has feeble rotatory power in aqueous solution. A mixture of equal proportions of *d*- and *l*-decahydroquinoline hydrochlorides has m. p. 274—275°, which is the melting point of synthetic decahydroquinoline hydrochlorides. T. H. P.

Scission of Decahydroquinoline into its Optical Antipodes. III. L. MASCARELLI (*Gazzetta*, 1915, **45**, *i*, 127—132. Compare preceding abstract).—The separation of *l*-decahydroquinoline *d*-bromocamphorsulphonate from the mother liquor remaining after the removal of the corresponding salt of the *d*-base presents some difficulty, treatment of this liquor with various solvents yielding fractions with m. p. varying between 165° and 200—205° and $[\alpha]_D^{25}$ between +59·04° and +78·21°. The largest fraction, m. p. 175°, $[\alpha]_D^{25}$ +61·3°, yields the *l*-base with the proper constants, and gives values in agreement with Pope and Read's rule (T., 1912, **101**, 760). It has been shown by these authors (T., 1912, **101**, 727) that, with bromocamphorsulphonates, the molecular rotation of the salt formed from the *d*-acid and *l*-base may be calculated with great accuracy from the known values for the ions, whilst when the ions are of the same sign, the calculated and observed values no longer agree. For decahydroquinoline *d*-bromocamphorsulphonates the calculated and observed values of $[M]_D$ are: (1) for the *l*-base, +272·5° and +276° respectively, and (2) for the *d*-base, +285·5° and +320° respectively.

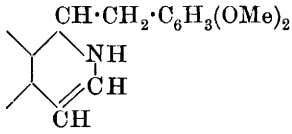
The formation of different fractions of *l*-decahydroquinoline *d*-bromocamphorsulphonate with varying properties is in agreement with the conclusion drawn by Kipping (T., 1905, **87**, 628), by Lowry and Magson (T., 1906, **89**, 1042), and by Pope and Read (T., 1914, **105**, 800), that salts of *d*-bromocamphorsulphonic acid exist in two dynamic isomeric forms.

The low values of the rotations of *d*- and *l*-decahydroquinolines are due to the small differences between the masses of the four substituent groups producing the asymmetry. T. H. P.

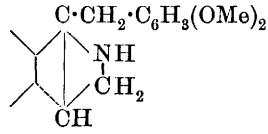
Preparation of Derivatives (Amides) of 2-Piperonylquinoline 4-carboxylic Acid and its Homologues. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P., 277,438; from *J. Soc. Chem. Ind.*, 1915, **34**, 249).—These amides are prepared by the usual methods, and like the amides of 2-phenylquinoline-4-carboxylic acid and its homologues (A., 1913, i, 92) they are tasteless. They do not promote the excretion of uric acid, however. J. C. W.

***iso*Quinoline Derivatives. VIII. Constitution of the Reduction Products of Papaverine (*cont.*). Constitution of Pavine.** FRANK LEE PYMAN (T., 1915, **107**, 176—187).—Papaverine,

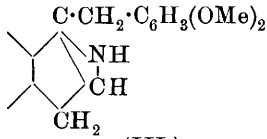
$C_{20}H_{21}O_4N$, yields two products on reduction, an amorphous base, tetrahydropapaverine, and a crystalline base, dihydropapaverine, $C_{20}H_{23}O_4N$, which has been termed pavine (compare Goldschmiedt, A., 1887, 163; 1899, i, 86; Pyman, T., 1909, **95**, 1610). The latter is a secondary base which could be represented by one of the three formulæ :—



(I.)

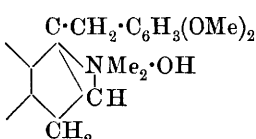


(II.)

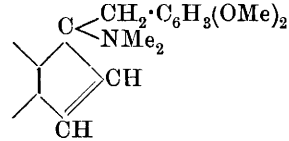


(III.)

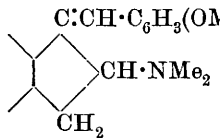
Of these, formula (I.) is excluded, since 1 : 2-dihydro*iso*quinolines are readily susceptible to oxidation and reduction, whereas pavine is very stable towards oxidising and reducing agents. The choice between (II.) and (III.) is rendered possible by a study of the degradation of the corresponding quaternary ammonium hydroxide by Hofmann's method. *N*-Methylpavine methohydroxide is converted into a *methine*, $C_{22}H_{27}O_4N$, from which, on oxidation, a *dicarboxylic acid*, $C_{22}H_{27}O_8N$, is obtained in good yield. The formation of this acid is clearly due to the oxidation of an unsaturated grouping, –CH:CH–, and since the acid contains the same number of carbon atoms as the methine, the molecule does not depend for its coherence on the ·CH:CH· group. Formula (II.) for pavine is therefore excluded. Formula (III.) for pavine leads to formula (IV.) for *N*-methylpavine methohydroxide, from which two possible methines, (V.) and (VI.), are derivable by Hofmann's reaction.



(IV.)



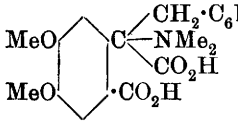
(V.)



(VI.)

Of these, the latter is impossible, since it would be degraded on oxidation to substances containing a smaller number of carbon atoms, whilst, on the other hand, the representation of the methine by

formula (V.) readily explains the production of a dicarboxylic acid of the annexed formula.



The evidence obtained from the oxidation of the methine is supported by the behaviour of the methine methiodide towards water and methyl alcohol, whereby trimethylamine hydriodide and two neutral *substances*, $C_{20}H_{22}O_5$ and $C_{21}H_{24}O_5$, are produced which contain four methoxyl and one hydroxyl and five methoxyl groups respectively. The ready elimination of the grouping $\cdot NMe_3I$ suggests that it is attached to a carbon atom of a negative group—in this case the benzene nucleus.

Pavinemethine is therefore 1-*dimethylamino*-1-*homoveratryl*-5 : 6-*dimethoxyindene*, whilst its degradation products, the substances $C_{20}H_{22}O_5$, $C_{20}H_{21}O_4Cl$, and $C_{21}H_{24}O_5$ are 1-*hydroxy*-, 1-*chloro*-, and 1-*methoxy*-1-*homoveratryl* 5 : 6-*dimethoxyindene* respectively. Oxidation of the latter compound yields two neutral *substances*, $C_{21}H_{24}O_7$ and $C_{21}H_{22}O_7$, a *monocarboxylic acid*, $C_{21}H_{24}O_8$, and a *dicarboxylic acid*, $C_{21}H_{24}O_9$, the detailed investigation of which is not yet completed.

N-Methylpavinemethine (1-homoveratryl-1-dimethylamino-5 : 6-dimethoxyindene) is prepared by digesting an aqueous solution of *N*-methylpavine methiodide with silver hydroxide, and treatment of the liquid with 50% aqueous potassium hydroxide. The base is purified by distillation and conversion into the *hydrochloride*, etc., and forms an apparently amorphous precipitate which becomes distinctly crystalline when preserved. On exposure to air, it passes into a horny mass which melts indefinitely at 50—95° (corr.), and contains $2H_2O$. The hydrochloride forms prismatic needles which contain $1\frac{1}{2}H_2O$ and, after drying at 100°, has m. p. 205—206° (corr.). The *aurichloride* decomposes at 156° (corr.). The *picrate*, yellow, prismatic needles, has m. p. 195—196° (corr.). The *methiodide* crystallises with $\frac{1}{2}H_2O$ [m. p. 174—175° (corr.)] or with $2\frac{1}{2}H_2O$ [m. p. 165—167° (corr.)].

N-Methylpavinemethine is readily oxidised by cold aqueous potassium permanganate in the presence of sulphuric acid. The *dicarboxylic acid* thus obtained forms colourless, prismatic needles, containing $5H_2O$. The air dried substance sinters at 80—100° and has m. p. 205—206° (corr. decomp.); after drying at 100°, however, it gradually melts at about 150°. The *hydrochloride*,

$$C_{22}H_{27}O_8N,HCl,H_2O,$$

needles, intumesces at 178° and then at 212° (corr.). The *aurichloride*, yellow prisms, decomposes at 240° (corr.). The *picrate*, yellow plates, has m. p. 137° (corr. decomp.).

N-Methylpavinemethine methiodide, when boiled with methyl alcohol, yields trimethylamine hydriodide and 1-*homoveratryl*-1 : 5 : 6-*trimethoxyindene*, prismatic needles, m. p. 130—131° (corr.) after previous softening. When a solution of the latter in acetone is oxidised with aqueous potassium permanganate at about 10°, somewhat capricious results are obtained; the following substances have been isolated:—*neutral substance*, $C_{21}H_{24}O_7$, pale yellow, prismatic needles, m. p. 141—142° (corr.); *neutral substance*, $C_{21}H_{22}O_7$, pale yellow clusters of prismatic rods, m. p. 170—172° (corr.); *monocarboxylic*

acid, $C_{21}H_{24}O_8$, colourless prisms, m. p. 220—222° (corr.) after softening at 210°; *dicarboxylic acid*, $C_{21}H_{24}O_9$, colourless needles or plates which melt at 206—207° (corr.) then lose gas, resolidify, and again melt at about 270°.

l-*Hydroxy*-1-*homoveratryl*-5 : 6-*dimethoxyindene*, colourless needles, m. p. 147—148° (corr.), and trimethylamine hydriodide are obtained by the action of boiling water on *N*-methylpavinemethine methiodide. The former substance is converted by boiling acetyl chloride into 2-*chloro*-1-*homoveratryl*-5 : 6-*dimethoxyindene*, prismatic needles, m. p. 118—220° (corr.). H. W.

Vat Dyes and Process for Making Same. Farbwerke vorm. Meister, Lucius, & Brüning. (U.S. Pat., 1,123,390; from *J. Soc. Chem. Ind.*, 1915, **34**, 221).—Dyes of the isatanthrene series are obtained by condensing an aromatic glycine with a halogenoanthraquinone, converting the resulting anthraquinonyl α-arylglycine ester by hydrolysis and dehydration into an *N*-arylanthrapyrrolecarboxylic acid, and treating this with a dehydrating agent. They dye cotton various tints of great fastness.

The simplest *isatanthrene*, $\begin{matrix} C_6H_4\cdot C{=}{=}C\cdot CO \\ CO{-}C_6H_3\cdot N\cdot C_6H_4 \end{matrix}$, is a reddish-brown powder which dissolves in pyridine with the same colour and in concentrated sulphuric acid with a deep reddish-violet colour, and dyes cotton red from a hyposulphite vat. J. C. W.

Synthesis by Means of Mixed Organo-metallic Derivatives of Zinc. γ-Chloroketones and their Transformation Products. II. Henri Wohlgemuth (*Ann. Chim.*, 1914, [ix], **2**, 403—465).—In the first part of the paper, which is a more detailed account of work already published (compare A., 1914, i, 929), two new compounds are described, namely, an *acetate*, b. p. 111—112°/15 mm., of ethyl γ-hydroxypyropyl ketone, and a *diacetate*, b. p. 121—124°/11 mm., of heptane-βε-diol.

In the second part of the paper an account is given of the behaviour of γ-chloroketones towards ammonia, hydroxylamine, hydrazine hydrate, and phenylhydrazine, and the resulting cyclic compounds are described. On heating ethyl γ-chloro-*n*-butyl ketone with alcoholic ammonia for thirty hours, the principal product is a *trimethylenic ketone*, b. p. 142—143°, only traces of basic products being formed (compare Lipp, A., 1896, i, 317; 1898, i, 379; Hielscher, A., 1898, i, 338). When ethyl γ-chloro-*n*-butyl ketone is added to a cold saturated aqueous solution of hydroxylamine hydrochloride, incompletely neutralised with potassium carbonate, and the mixture stirred frequently during eight days, on extraction with ether, the corresponding *oxime* is obtained. If this oxime is heated with pyridine in alcohol under a reflux for six hours, or if the original ketone is added to a saturated solution of hydroxylamine hydrochloride, completely neutralised with potassium carbonate, and the mixture heated on a water-bath for six hours, 6-*methyl*-3-*ethyl*-5 : 6-*dihydro*isooxazine, $CH\begin{matrix}\diagup CEt{-}{-}NH\diagdown \\ CH_2\cdot CHMe\diagup O\end{matrix}$, b. p. 118—119°/13 mm., is obtained as a

colourless, mobile liquid. It is very soluble in water, reduces ammoniacal silver nitrate in the cold, and Fehling's solution on boiling. It reacts with methyl iodide, phenylcarbimide, and benzenesulphonyl chloride, the products obtained being all uncrystallisable oils, but with picrolonic acid (4-nitro-1-*p*-nitrophenyl-3-methylpyrazolone) it gives a *picrolonate*, prisms, m. p. 148°. The *iso*oxazine has D_4^{25} 0·9893; n_α^{25} 1·49035; n_D^{25} 1·49394; n_β^{25} 1·50193 and its behaviour towards magnesium ethyl bromide indicates the presence of an :NH group (compare Zerewitinov, A., 1908, i, 593). Ethyl γ-chloropropyl ketone yields with hydroxylamine under similar conditions *3-ethyl-5 : 6-dihydro*isoo*xazine*, $CH\begin{matrix}\diagup\\\diagdown\end{matrix}\begin{matrix}CEt{-}NH\\CH_2\cdot CH_2\end{matrix}\rangle O$, b. p. 130—131°/13 mm.

The γ-chloroketones readily react with hydrazine hydrate in 50% aqueous solution, giving cyclic derivatives possessing basic properties and giving crystalline compounds with hydrogen chloride, *iso*cyanic acid, and benzoyl chloride. Thus ethyl γ-chloro-*n*-butyl ketone gives with hydrazine hydrate, *6-methyl-3-ethyltetrahydropyridazine*,

$$CH_2\begin{matrix}\diagup\\\diagdown\end{matrix}\begin{matrix}CEt{=}N\\CH_2\cdot CHMe\end{matrix}\rangle NH,$$

b. p. 77·5—78°/11 mm., a pale yellow, mobile liquid, rapidly becoming coloured on exposure to air, which gives a *hydrochloride*, m. p. 117°, and a *benzoyl* derivative, m. p. 56°.

Ethyl γ-chloropropyl ketone with hydrazine hydrate yields *3-ethyltetrahydropyridazine*, $CH_2\begin{matrix}\diagup\\\diagdown\end{matrix}\begin{matrix}CEt{=}N\\CH_2\cdot CH_2\end{matrix}\rangle NH$, a colourless liquid, b. p 77°/13 mm., giving a *hydrochloride*, which is exceedingly hygroscopic and gives an unstable platinichloride, a *benzoyl* derivative, an oil, b. p. 202°/12·5 mm. With potassium cyanate a concentrated aqueous solution of the hydrochloride yields *1-carbamyl-3-ethyltetrahydropyridazine*, $CH_2\begin{matrix}\diagup\\\diagdown\end{matrix}\begin{matrix}CEt{=}N\\CH_2\cdot CH_2\end{matrix}\rangle N\cdot CO\cdot NH_2 + H_2O$, m. p. 81°, which is also obtained by boiling ethyl γ-chloropropyl ketone semicarbazone with pyridine in absolute alcohol on a water-bath for six hours.

On warming the γ-chloroketones with phenylhydrazine in alcohol, the corresponding *N*-phenyltetrahydropyridazines are obtained, as solid compounds, insoluble in water, soluble in mineral acids, and giving crystalline derivatives with phenylcarbimide. Thus ethyl γ-chloro-*n*-butyl ketone yields *1-phenyl-6-methyl-3-ethyltetrahydropyridazine*, $CH\begin{matrix}\diagup\\\diagdown\end{matrix}\begin{matrix}CEt{-}NH\\CH_2\cdot CHMe\end{matrix}\rangle NPh$, b. p. 205—207°/11 mm., m. p. 80°, giving with phenylcarbimide, *2-phenylcarbamyl-1-phenyl-6-methyl-3-ethyltetrahydropyridazine*, $CH\begin{matrix}\diagup\\\diagdown\end{matrix}\begin{matrix}CEt\cdot N(CO\cdot NHPh)\\CH_2\text{———}CHMe\end{matrix}\rangle NPh$, m. p. 152—153°.

Ethyl γ-chloropropyl ketone yields *1-phenyl-3-ethyltetrahydropyridazine*, $CH\begin{matrix}\diagup\\\diagdown\end{matrix}\begin{matrix}CEt{-}NH\\CH_2\cdot CH_2\end{matrix}\rangle NPh$, b. p. 212—214°/16 mm., m. p. 77—78°, giving *2-phenylcarbamyl-1-phenyl-3-ethyltetrahydropyridazine*,

$$CH\begin{matrix}\diagup\\\diagdown\end{matrix}\begin{matrix}CEt\cdot N(CO\cdot NHPh)\\CH_2\text{———}CH_2\end{matrix}\rangle NPh,$$

m. p. 158°, with phenylcarbimide. W. G.

Action of Acetic Anhydride on Some Benzylideneanthranilic Acids. IV. JOHN B. EKELEY and CHARLES F. POE (*J. Amer. Chem. Soc.*, 1915, **37**, 582—586).—In earlier papers (Ekeley and Dean, A., 1912, i, 211; Ekeley and Clinton, A., 1913, i, 395; Ekeley and Slater, A., 1914, i, 576) a number of oxazines were described which were obtained by the action of acetic anhydride on benzylideneanthranilic acids. As the method employed failed to yield the expected oxazines with anisaldehyde and piperonal, further experiments have been carried out, and it has been found that these oxazines can be prepared by heating the benzylideneanthranilic acid with acetic anhydride in xylene solution, and subsequently distilling off the xylene and cooling the residue to 0°.

o-*Toluylideneanthranilic acid*, m. p. 143°, forms white crystals and yields 4-*acetyl*-3-o-*tolyldihydro*-2 : 4-*benzoxazine*-1-*one*,

$$C_6H_4\begin{<}CO—O\\NAc\cdot CH\cdot C_6H_4Me\end{>}$$

m. p. 166°, which crystallises in colourless prisms.

Dibromosalicylideneanthranilic acid, m. p. 176°, forms scarlet needles, and furnishes colourless prisms of 4-*acetyl*-3-*acetyldibromophenyldihydro*-2 : 4-*benzoxazine*-1-*one*, m. p. 153°, together with a small quantity of an intensely yellow, crystalline substance, m. p. 274°, which is probably 4-*acetyl*-3-*dibromophenyldihydro*-2 : 4-*benzoxazine*-1-*one*.

1 : 4-α-*Hydroxynaphthylideneanthranilic acid*, m. p. 195°, crystallises in maroon-coloured, microscopic needles, and gives 4-*acetyl*-3-*acetyl*-α-*hydroxynaphthyldihydro*-2 : 4-*benzoxazine*-1-*one*, m. p. 238°, which forms colourless, microscopic needles.

Anisylideneanthranilic acid, m. p. 146°, yields 4-*acetyl*-3-p-*methoxyphenyldihydro*-2 : 4-*benzoxazine*-1-*one*, m. p. 118°, which forms colourless crystals.

Piperonylideneanthranilic acid, m. p. 196°, forms yellow crystals, and furnishes 4-*acetyl*-3-mp-*methylenedioxyphenyldihydro*-2 : 4-*benzoxazine*-1-*one*, m. p. 126°.

Methylvanillylideneanthranilic acid, m. p. 163°, crystallises in bright yellow needles, and gives 4-*acetyl*-3-mp-*dimethoxyphenyldihydro*-2 : 4-*benzoxazine*-1-*one*, m. p. 106°.

m-*Methoxysalicylideneanthranilic acid*, m. p. 113°, forms red needles, and yields 4-*acetyl*-3-m-*acetoxy*-p-*methoxyphenyldihydro*-2 : 4-*benzoxazine*-1-*one*, m. p. 187°.

4-*Acetyl*-3-p-*acetoxy*-m-*methoxyphenyldihydro*-2 : 4-*benzoxazine*-1-*one*, m. p. 141°, obtained by the action of acetic anhydride on vanillylideneanthranilic acid in presence of xylene, differs from the product obtained by heating the acid directly with excess of acetic anhydride (A., 1912, i, 212), and it is considered that the latter was not pure.

E. G.

Interaction of Ammonia and Methylamine with 2 : 3 : 4-Trinitrodimethylaniline. P. VAN ROMBURGH and MISS D. W. WENSINK (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1034—1036).—2 : 3 : 4-Trinitrodimethylaniline, m. p. 154°, has a very mobile nitro-group in position 3 Thus, alcoholic ammonia causes the separation of 2 : 4-*dinitro*-m-*phenylene*-as-*dimethyldiamine*, pale yellow crystals, m. p. 162°,

and methylamine causes the separation of 2 : 4-*dinitro*-m-*phenylene-trimethyldiamine*, $\cdot NHMe \cdot C_6H_2(NO_2)_2 \cdot NMe_2$, m. p. 125°, from alcoholic solutions. If the original substance, or these derivatives, be heated under pressure with these reagents, the dimethylamino-group is also attacked. Thus, ammonia yields 2 : 4-dinitro-*m*-phenylenediamine, pale brown or orange needles from methyl salicylate, decomp. 250°, (Barr, A., 1888, 822), and dimethylamine, whereas methylamine produces 2 : 4-dinitro-*m*-phenylenedimethyldiamine,

$$C_6H_2(NO_2)_2(NHMe)_2,$$

m. p. 169° (Blanksma, A., 1908, i, 157). J. C. W.

Preparation of 5(4)-Methyl-4(5)-arylaminomethylglyoxalines. O. Gerngross (D.R.-P., 278,884; from *J. Soc. Chem. Ind.*, 1915, **34**, 250).—Compounds of the above type (compare this vol., i, 29) may be prepared by the action of 5(4)-methyl-4(5)-chloromethylglyoxaline or its salts on primary aromatic amines. They increase the blood pressure, act as antiseptics towards lower organisms, but are not so toxic as β-amino-4-ethylglyoxaline. J. C. W.

Synthesis of Thiohydantoin. III. Shigeru Komatsu (*Mem. Coll. Sci. Kyōto*, 1914, **1**, 69—79).—When certain α-amino-acids are heated with potassium thiocyanate in the presence of acetic anhydride, the corresponding 4-substituted 2-thio-3-acetylhydantoins are produced, although the yield in the case of α-amino*iso*butyric acid is only 4%. It was thought that the 3-substituted 2-thiohydantoin would be formed from sarcosine, but it was found that this acid does not condense with thiocyanates in the presence of acetic anhydride (compare Johnson and Scott, A., 1913, i, 1105), although the hydrochloride of sarcosine ethyl ester reacts with potassium thiocyanate in alcoholic solution (compare phenylglycine and its ester, Wheeler and Brautlecht, A., 1911, i, 501). The failure of *N*-substituted α-amino-acids to undergo condensation is shared by the dicarboxylic acids, aspartic and glutamic (Johnson and Guest, A., 1913, i, 316, 807). These authors explained the fact by assuming the deamidation of the amino-acids, basing their views on an estimation of the ammonium chloride formed during the interaction of potassium thiocyanate, aspartic acid, and acetic anhydride. The author has repeated this work and finds that the yield of ammonium chloride depends on the amount of potassium thiocyanate, and not on the aspartic acid.

The desulphurisation of thiohydantoins, which is effected by several reagents in presence of water, is explained by assuming that the elements of water are first attached to the :C:S linking, followed by the elimination of hydrogen sulphide, thus,

$$SC\langle^{NPh\cdot CO}_{NH-CHPh} \rightarrow SH(OH)C\langle^{NPh\cdot CO}_{NH-CHPh} \rightarrow OC\langle^{NPh\cdot CO}_{NH-CHPh}$$

(see below). The analogous conversion of thiocarbanilide into carbanilide would be explained in the same way.

Equimolecular proportions of leucine and potassium thiocyanate were heated with acetic anhydride on the water-bath, and, on pouring

the resulting yellow solution into water, 2-*thio*-3-*acetyl*-4-iso*butyl*-*hydantoin*, $NH<^{CO\cdot CH\cdot CH_2\cdot CHMe_2}_{CS\cdot NAc}$ separated, in colourless, silky scales, m. p. 112—113°. This was hydrolysed by concentrated hydrochloric acid to 2-*thio*-4-iso*butylhydantoin*, which forms silky scales, m. p. 169—170°. Similarly, α-amino*iso*butyric acid produced, finally, 2 *thio*-4-*dimethylhydantoin*, $C_5H_8ON_2S$, in colourless needles, m. p. 163—164°, but the yield was only about 4%. α-Amino*iso*valeric acid yielded 2-*thio*-3-*acetyl*-4-iso*propylhydantoin*, needles, m. p. 98—99°, and subsequently 2-*thio*-4-iso*propylhydantoin*, $NH<^{CO\cdot CH\cdot CHMe_2}_{CS\cdot NH}$, which forms colourless plates, m. p. 129—130°. α-Aminophenylacetic acid gave rise to 2-*thio*-3-*acetyl*-4-*phenylhydantoin*, m. p. 185—186°, and to 2-*thio*-4-*phenylhydantoin*, colourless needles, m. p. 211—212° (decomp.).

The hydrochloride of sarcosine ethyl ester was heated with potassium thiocyanate and alcohol and thereby converted into 2-*thio*-3-*methyl*-*hydantoin*, $NH<^{CO\cdot CH_2}_{CS\cdot NMe}$, which forms yellow scales, m. p. 214—215°.

2-*Thio*-1-*phenyl*-3-*methylhydantoin*, $NPh<^{CO\cdot CH_2}_{CS\cdot NMe}$, was also prepared, by the action of phenylthiocarbimide on sarcosine. It forms pale yellow plates, m. p. 150—151°. α-Aminophenylacetic acid and phenylthiocarbimide yielded a reddish-brown substance, m. p. 155—156°, insoluble in hot water, and also 2-*thio*-1 : 4-*diphenylhydantoin*, which crystallises from hot water in needles, m. p. 223—224°, and yields 1 : 4-diphenylhydantoin on boiling with dilute chloroacetic acid (see above). J. C. W.

Constitution of Acetylacetonethiocarbamide [2-Thio-4 : 6-dimethyldihydropyrimidine]. William J. Hale and Arthur G. Williams (*J. Amer. Chem. Soc.*, 1915, **37**, 594—600).—An account of a study of the constitution of the two modifications of acetylacetonecarbamide has been given by Hale (A., 1914, i, 207). Evans (A., 1894, i, 111) has stated that thiocarbamide also condenses with acetylacetone with formation of two distinct products. These compounds have now been investigated.

When thiocarbamide is treated with acetylacetone in accordance with Evans's method, acetylacetonethiocarbamide, m. p. 210°, is obtained in the form of pale yellow prisms; if light petroleum is added to a solution of this compound in chloroform, the substance is precipitated as small, colourless crystals. When acetylacetonethiocarbamide is heated with chloroacetic acid, it is converted into acetylacetonecarbamide, m. p. 198°.

By the condensation of methylthiocarbamide with acetylacetone in presence of hydrochloric acid, the *hydrochloride* of 2-*thio*-3 : 4 : 6-*trimethyl*-2 : 3-*dihydropyrimidine* is produced, which forms yellow prisms. When this salt is treated with alkali hydroxide, it yields the free *pyrimidine*, $CH<^{CMe=N}_{CMe\cdot NMe}>CS$, m. p. 156·5°, which forms small needles and is not affected by prolonged boiling with hydrochloric

acid. By the action of chloroacetic acid on the pyrimidine, it is converted into 3 : 4 : 6-trimethyl-2 : 3-dihydropyrimid-2-one (Hale, *loc. cit.*).

When ψ-methylthiocarbamide is condensed with acetylacetone in presence of potassium hydroxide, 2-methylthiol-4 : 6-dimethylpyrimidine (Wheeler and Jamieson, A., 1904, i, 942) is produced, which, when boiled with concentrated hydrobromic acid, is converted into 4 : 6-dimethyldihydropyrimid-2-one. 2-Methylthiol-4 : 6-dimethylpyrimidine can be readily prepared by the action of methyl iodide on acetylacetone thiocarbamide in presence of sodium methoxide. Attempts were made to methylate acetylacetonethiocarbamide by means of diazomethane, but without success.

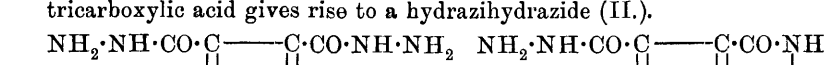
From the results of this work, it is considered that acetylacetonethiocarbamide may be regarded as 2-thio-4 : 6-dimethyl-2 : 5-dihydropyrimidine, $CH_2<^{CMe:N}_{CMe:N}>CS$, in equilibrium with a small proportion of 2-thio-4 : 6-dimethyl-2 : 3-dihydropyrimidine,

$$CH<^{CMe=N}_{CMe\cdot NH}>CS.$$

E. G.

Hydrazides and Azoimides of Organic Acids. XXX. Formation of Hydrazihydrazides and Hydraziazoimides of Tribasic Acids. Theodor Curtius (*J. pr. Chem.*, 1915, [ii], **91**, 39—102; compare this vol., i, 124).—This paper deals with the hydrazides and azoimides of pyrazoline-3 : 4 : 5-tricarboxylic, pyrazole-3 : 4 : 5-tricarboxylic, trimesic, and hemimellitic acids.

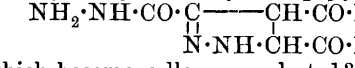
In addition to the normal trihydrazide (I.), pyrazole-3 : 4 : 5-tricarboxylic acid gives rise to a hydrazihydrazide (II.).



(I.) (II.)

Trimesic acid forms only the normal trihydrazide, whilst hemimellitic acid yields a hydrazihydrazide, $NH_2\cdot NH\cdot CO\cdot C_6H_3<^{CO\cdot NH}_{CO\cdot NH}$.

From these results the author draws the conclusion that only those tribasic acids containing two carboxyl groups in the 1 : 2-positions are capable of giving rise to hydrazihydrazides.

[With Edmund Bourcart.]—Ethyl pyrazoline-3 : 4 : 5-tricarboxylate, prepared by the condensation of ethyl diazoacetate and ethyl fumarate, crystallises in short, colourless needles, probably belonging to the rhombic system, m. p. 97°, D^{22} 1·2073° (compare Buchner and Heide, A., 1901, i, 232). It reacts with hydrazine hydrate in alcoholic solution at the ordinary temperature, yielding *pyrazoline*-3 : 4 : 5-*tricarboxylhydrazide*,  , crystallising in needles, which become yellow or red at 130—140°, m. p. 148° (decomp.); the following salts of the hydrazide are described: the *hydrochloride*, B,3HCl, is very hygroscopic, and decomposes when kept; *sulphate*; *nitrate*; *picrate*, small, yellow needles; *platinichloride*, $C_{12}H_{30}O_6N_{16}Cl_{12}Pt_3$, and *cadmichloride*, $C_{12}H_{24}O_6N_{16}Cl_6Cd_3$. The hydr-

azide forms *double salts* with sodium sulphate and disodium hydrogen phosphate. When shaken with benzaldehyde in aqueous solution, it yields a white, non-crystalline *tribenzylidene* derivative,

$$C_3N_2H_3(CO\cdot NH\cdot N{:}CHPh)_3;$$

the *tri*-p-*nitrobenzylidene* derivative forms a white powder, which becomes strongly electric when rubbed.

The following derivatives are also described: *tri*-o-*hydroxybenzylidene*, which becomes red at 130°, and melts with decomposition at a higher temperature; *trivanillylidene*, m. p. 139° (decomp.); *tripiperonylidene*; *tricinnamylidene*, citron-yellow, microcrystalline precipitate; *trifurfurylidene*; *triisopropylidene* (from acetone). The *triacetyl* derivative, $C_3N_2H_3(CO\cdot NH\cdot NHAc)_3$, is a colourless powder, m. p. 140° (decomp.), with previous reddening at 100—130°.

Pyrazoline-3 : 4 : 5-*tricarboxylazoimide*, $C_3N_2H_3(CO\cdot N_3)_3$, prepared from the trihydrazide and nitrous acid in cold aqueous solution, forms a viscid, transparent, oily mass, which explodes when heated, and reacts with aniline and *p*-toluidine in ethereal solution, yielding the corresponding *trianilide* and *tri*-p-*toluidide* as white, amorphous precipitates.

Ethyl pyrazoline-3 : 4 : 5-*tricarbamate* is obtained in an impure condition as a viscid, light brown mass by heating the triazoimide in alcoholic solution, and when heated with concentrated hydrochloric acid is converted into 3 : 4 : 5-*triaminopyrazoline*,

$$\begin{array}{l} NH_2\cdot C\text{——}CH\cdot NH_2 \\ \quad\|\qquad\quad| \\ \quad N\cdot NH\cdot CH\cdot NH_2 \end{array},$$

which could not be isolated in a pure condition and was therefore characterised by the preparation of the *picrate*, $B,3C_6H_2(NO_2)_3\cdot OH$, short, yellow, flat, monoclinic needles, m. p. about 180° (decomp.), D^{22} 1·757.

The *hydrochloride* of the triamine is also described, but could not be obtained in a pure condition; on diazotisation it couples with β-naphthol and resorcinol, yielding dark brown *azo-dyes*.

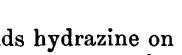
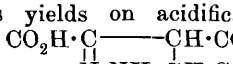
The crude pyrazoline-3 : 4 : 5-tricarboxylhydrazide, obtained by the interaction of hydrazine hydrate and ethyl pyrazoline-3 : 4 : 5-tricarboxylate in alcoholic solution, contains a small amount of a white product which is insoluble in water and reacts with benzaldehyde in dilute hydrochloric acid, yielding benzaldazine together with a *benzylidene* compound, m. p. above 220° (decomp.); it probably consists of a mixture of *pyrazoline*-3 : 4 : 5-*tricarboxylhydrazihydrazide*,

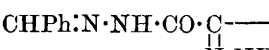
$$\begin{array}{l} NH_2\cdot NH\cdot CO\cdot C\text{——}CH\cdot CO\cdot NH \\ \quad\|\qquad\quad| \\ \quad N\cdot NH\cdot CH\cdot CO\cdot NH' \end{array}$$

and its *hydrazine* salt, whilst the *benzylidene* compound, m. p. above 220°, probably has the formula:

$$\begin{array}{l} CHPh{:}N\cdot NH\cdot CO\cdot C\text{——}CH\cdot CO\cdot NH \\ \quad\|\qquad\quad| \\ \quad N\cdot NH\cdot CH\cdot CO\cdot NH' \end{array}$$

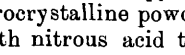
In the preparation of pyrazoline-3 : 4 : 5-tricarboxylazoimide by the addition of sodium nitrite to a cold hydrochloric acid solution of the corresponding hydrazide, if the hydrochloric acid is not in excess and the triazoimide at once removed by extraction with ether, a light orange-coloured substance is produced, which possesses both acid and

basic properties, yields hydrazine on hydrolysis with mineral acids and is considered to be a *pyrazoline*-3 : 4 : 5-*hydraziazoimide* of the following constitution,  . It gives an intense brownish-violet coloration with ferric chloride, and with silver nitrate in ammoniacal solution forms an unstable *silver* salt; its solution in aqueous alkalis yields on acidification *pyrazoline*-3 : 4 : 5-*hydrazi-carboxylic acid*,  .

[With Ludwig Hans Heynemann.]—Ethyl pyrazole-3 : 4 : 5-tricarboxylate, prepared by the condensation of ethyl diazoacetate with ethyl acetylenedicarboxylate at a low temperature, forms stout crystals or needles, m. p. 68° (compare Buchner and Heide, A., 1901, i, 232), and is converted by aqueous ammonia into the corresponding amide. When treated with hydrazine hydrate in alcoholic solution at the ordinary temperature, it yields *pyrazole*-3 : 4 : 5-*tricarboxylhydrazide*, which forms a white, microcrystalline powder, decomposing above 300°, and is transformed by boiling with water into pyrazole-3 : 4 : 5-tricarboxylhydrazihydrazide (see below). The trihydrazide condenses with benzaldehyde in aqueous solution, yielding a *tribenzylidene* derivative,  ;

the *tri*-o-*hydroxybenzylidene* and *tri*-m-*nitrobenzylidene* derivatives are also described.

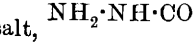
The *tricinnamylidene* derivative, obtained together with cinnamaldazine and the *cinnamylidene* derivative of *pyrazole*-3 : 4 : 5-*tricarboxylhydrazide* (not isolated in a pure condition) by shaking cinnamaldehyde with an aqueous solution of pyrazole-3 : 4 : 5-tricarboxylhydrazide, forms a yellow, microcrystalline powder.

On treatment with nitrous acid the trihydrazide is converted into *pyrazole*-3 : 4 : 5-*tricarboxylazoimide*,  , a crystalline solid, which explodes when heated and reacts with aniline in ethereal solution, yielding *pyrazole*-3 : 4 : 5-*tricarboxylanilide*, radiating clusters of colourless needles, m. p. above 270°.

Attempts to prepare 3 : 4 : 5-triaminopyrazole by boiling the triazoimide with alcohol and hydrolysing the resulting impure *urethane* were unsuccessful.

When heated for several hours with hydrazine hydrate in alcoholic solution, ethyl pyrazole-3 : 4 : 5-carboxylate yields a mixture of *pyrazole*-3 : 4 : 5-*tricarboxylhydrazihydrazide*,

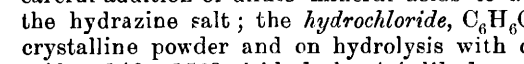


and its *hydrazine* salt,  .

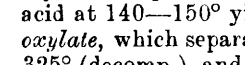
The latter salt is readily isolated by crystallising the mixture from water; it separates first of all as a gelatinous mass and then crystallises in needles.

The pyrazole-3 : 4 : 5-tricarboxylhydrazihydrazide, mentioned above, possesses both acid and basic properties, and is best obtained by the careful addition of dilute mineral acids to a hot aqueous solution of the hydrazine salt; the *hydrochloride*, $C_6H_6O_3N_6,HCl$, forms a white, crystalline powder and on hydrolysis with concentrated hydrochloric acid at 140—150° yields *hydrazine dihydrogen pyrazole*-3 : 4 : 5-*tricarboxylate*, which separates in lustrous, white, silky needles, m. p. above 325° (decomp.), and forms a gelatinous *silver* salt.

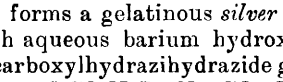
On treatment with aqueous barium hydroxide, the hydrochloride of pyrazole-3 : 4 : 5-tricarboxylhydrazihydrazide gives rise to a *barium* salt,



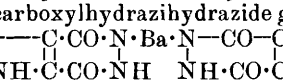
with benzaldehyde it forms a white, flocculent *benzylidene* derivative,



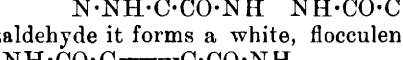
Pyrazole-3 : 4 : 5-*tricarboxylhydraziazoimide*,



obtained as a yellow, flocculent precipitate, by the addition of sodium nitrite to an aqueous solution of the corresponding hydrazihydrazide hydrochloride, reacts with aniline to form the *hydrazianilide*,

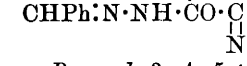


when boiled with water it is converted into the *carbamide*,



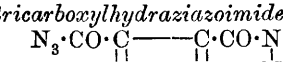
which, however, was not isolated in a pure condition.

The hydraziazoimide is hydrolysed by cold dilute aqueous sodium hydroxide to hydrazoic acid and *pyrazolehydrazicarboxylic acid*,



which separates as an amorphous powder on acidifying the alkaline solution.

The *hydraziurethane*,



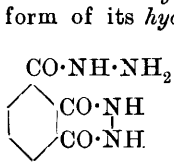
prepared by boiling the hydraziazoimide in alcoholic solution, becomes brown at 220°, and melts with decomposition at a higher temperature.

[With Aloys Joseph Schmitz.]—Ethyl trimesate reacts with hydrazine hydrate in boiling alcoholic solution, yielding *trimesylhydrazide*, $C_6H_3(CO\cdot NH\cdot NH_2)_3$, which forms microscopic, tabular crystals (decomp. above 300°), and gives a *hydrochloride*, B,3HCl, crystallising with $1H_2O$ in efflorescent, lustrous needles or platelets; the *tribenzylidene* derivative, $C_6H_3(CO\cdot NH\cdot N{:}CHPh)_3$, crystallises with $1H_2O$, and has m. p. 224°.

The *triazoimide*, $C_6H_3(CO\cdot N_3)_3$, obtained as a white, flocculent precipitate by treating a cold dilute hydrochloric acid solution of the hydrazide with the calculated amount of sodium nitrite, is converted by the action of aniline and alcohol into *trimesanilide*, m. p. 118—120° (decomp.) and *ethyl benzene*-1 : 3 : 5-*tricarbamate* (*tri*-N-*carbethoxy*-1 : 3 : 5-*triaminobenzene*), $C_6H_3(NH\cdot CO_2Et)_3$, m. p. 110—111° respectively.

When heated with dilute hydrochloric acid at 100° the last-named compound gives rise to a *substance*, m. p. 172—173°, which is possibly a diurethane, $NH_2 \cdot C_6H_3(NH \cdot CO_2Et)_2$; hydrolysis with concentrated hydrochloric acid at 115—120° yields phloroglucinol.

Hemimellitoylhydrazihydrazide (annexed formula), obtained in the form of its *hydrazine* salt (yellowish-red crystals, m. p. above 300°) by heating ethyl hemimellitate with hydrazine hydrate in alcoholic solution, cystallises in yellow, microscopic, felted needles, m. p. above 300°, and yields a white, crystalline *hydrochloride*; the *benzylidene* derivative, $CHPh{:}N \cdot NH \cdot CO \cdot C_6H_3\langle \begin{matrix} CO \cdot NH \\ | \\ CO \cdot NH \end{matrix}$, forms a white, microcrystalline powder, m. p. above 300°. On treatment with nitrous acid it is converted into *hemimellitoylhydraziazoimide*,



$$N_3 \cdot CO \cdot C_6H_3\langle \begin{matrix} CO \cdot NH \\ | \\ CO \cdot NH \end{matrix},$$

which reacts with aniline to form *hemimellitoylhydrazianilide* (yellow, crystalline powder, m. p. above 300°), and with alcohol yielding the *urethane*, $CO_2Et \cdot NH \cdot C_6H_3\langle \begin{matrix} CO \cdot NH \\ | \\ CO \cdot NH \end{matrix}$, a grey, crystalline powder, m. p. above 300°. When boiled with water, the hydraziazoimide gives rise to a *carbamide*, $\begin{matrix} NH \cdot CO \\ | \\ NH \cdot CO \end{matrix}\rangle C_6H_3 \cdot NH \cdot CO \cdot NH \cdot C_6H_3\langle \begin{matrix} CO \cdot NH \\ | \\ CO \cdot NH \end{matrix}$, crystallising in slender, monoclinic columns, m. p. above 300°. Both the preceding carbamide and urethane are hydrolysed by concentrated hydrochloric acid at 100° to *o*-aminophthaloylhydrazide,

$$NH_2 \cdot C_6H_3\langle \begin{matrix} CO \cdot NH \\ | \\ CO \cdot NH \end{matrix},$$

(Curtius and Semper, A., 1913, i, 472), which is converted by prolonged heating with hydrochloric acid at 145—150° into *m*-aminobenzoic acid.

Hydrazine dihydrogen hemimellitate, obtained together with hemimellitoylhydrazihydrazide by heating hydrazine hydrate with hemimellitic acid, crystallises with $3H_2O$ in colourless needles, m. p. 173°.

F. B.

The Catalytic Reduction of Indigotin and of Vat-dyes. André Brochet (*Compt. rend.*, 1915, **160**, 306—308; compare A., 1914, i, 1069).—Indigotin in suspension in water or in a dilute solution of sodium hydroxide in the presence of active nickel, readily undergoes reduction to its leuco-base on passing hydrogen through the suspension. The reduction is exceedingly rapid at 60—80° and is more rapid when sodium hydroxide is present than in its absence. The synthetic indigo paste is reduced more rapidly than the material sold in the dry state. The process forms a ready method of obtaining indigo-white in a comparatively pure state, by concentrating the resulting liquid, after filtration, in a vacuum. W. G.

Preparation of Amino-Derivatives of 2-Phenylquinoline-4-carboxylic Acid. Chemische Fabrik auf Aktien (vorm. E. Schering). (D.R.-P., 279,195; from *J. Soc. Chem. Ind.*, 1915, **34**, 249.)—These

are prepared by reducing the 2-*o*-, -*m*- or -*p*-nitrophenylquinoline-4-carboxylic acid, by the interaction of aniline, pyruvic acid and an aminobenzaldehyde in alcoholic solution, or by heating an alcoholic solution of the condensation product of aniline and an aminobenzaldehyde with pyruvic acid. The new products are superior to 2-phenylquinoline-4-carboxylic acid (A., 1913, i, 92) for therapeutic purposes, for they do not cause such an increase in the separation of uric acid.

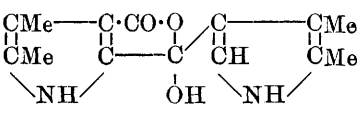
J. C. W.

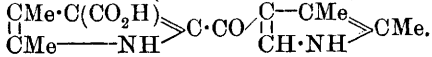
Pyrranthraquinones (Pyrrindoquinones). O. Piloty, Karl Wilke, and Alfred Blömer (*Annalen*, 1914, **407**, 1—42; compare Piloty and Wilke, A., 1913, i, 767).—In order to indicate a suggested analogy to the anthracene compounds, the authors propose that the substances pyrrindole and pyrrindoquinone should be re-named pyrranthracene and pyrranthraquinone respectively.

The yield of tetramethylpyrrindoquinone is increased from 30 to 52% by heating 2 : 3-dimethylpyrrole-4-carboxylic acid with twice or thrice its weight of acetic anhydride at 170—175° for 6 hours.

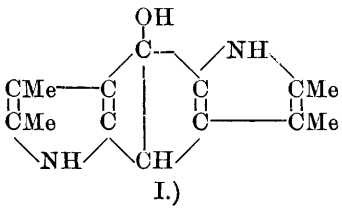
The present paper deals mainly with the preparation of pyrrindole derivatives from 1-methyl-2-ethylpyrrole-4-carboxylic acid and with the examination of the reaction whereby pyrroles, unsubstituted in the α-position and containing a carboxyl group in the β-position, yield pyrrindoquinones by treatment with acetic anhydride. It is very probable that the first product is a mixed anhydride, which then decomposes in the manner of such substances, yielding acetic anhydride and the anhydride of the pyrrole-4-carboxylic acid; the latter yields the pyrrindoquinone by the loss of water. This explanation is supported by the following evidence. (1) The same pyrrindoquinone is formed when benzoic anhydride is used instead of acetic anhydride. (2) In the preparation of tetramethylpyrrindoquinone from 2 : 3-dimethylpyrrole-4-carboxylic acid and acetic anhydride, the mother liquor, from which the quinone has been separated, contains a *substance*, small needles, m. p. about 180° (decomp.), which yields acetic acid and tetramethylpyrrindoquinone by heating, is hydrolysed by hot aqueous sodium hydroxide, yielding 2 : 3-dimethylpyrrole-4-carboxylic acid, and has approximately the composition, $C_9H_{11}O_3N$, of the mixed acid anhydride, $\begin{matrix}CMe{:}CMe\\ |\\ NH{-}{-}CH\end{matrix}\!\!>C\cdot CO\cdot O\cdot COMe$. The mixed acid anhydride has been synthesised by treating equal molecular quantities of 2 : 3-dimethylpyrrole-4-carboxylic acid and acetyl chloride with an excess of pyridine in dry ether, and also from acetyl chloride and a suspension of the potassium salt in cold petroleum. It has m. p. about 180° when heated slowly, but by rapid heating it melts at about 140°, resolidifies, melts again at about 180° (decomp.), and finally yields tetramethylpyrrindoquinone. In the second method of preparation a *substance*, colourless, rhombic plates, m. p. 236°, is also formed which is identical with that produced from the mixed anhydride at 140° and is proved to be 2 : 3-*dimethylpyrrole*-4-*carboxylic anhydride*, $(C_7H_8ON)_2O$, by its synthesis from potassium 2 : 4-dimethylpyrrole-4-carboxylate and phosphoryl chloride in boiling petroleum.

As is to be expected from the course of the reaction described above, 5-*acetyl*-2 : 3-*dimethylpyrrole*-4-*carboxylic acid*, $C_9H_{11}O_3N$, leaflets, m. p. 277·5° (*ethyl* ester, m. p. about 125°), obtained by heating a benzene solution of ethyl 1-acetyl-2 : 3-dimethylpyrrole-4-carboxylate at 270—280° and hydrolysing the product, does not yield a pyrrindoquinone by treatment with acetic anhydride. Tetramethylpyrrindoquinone is obtained in even better yield by employing the chlorides of phosphorus. By careful treatment with the pentachloride, 2 : 3-dimethylpyrrole-4-carboxylic acid in petroleum is converted into its anhydride, which, without being isolated, gives a 79·6% yield of the quinone by boiling with acetic anhydride. Finally, the interaction of 2 : 3-dimethylpyrrole-4-carboxylic acid and about 10 parts of phosphorus trichloride at the ordinary temperature gives the quinone in 85% yield. A by-product in the last method is a *substance*, $C_{16}H_{22}O_4N_2$, m. p. about 250° (decomp.), citron yellow plates and prisms with green and orange-yellow reflex, which is insoluble in cold aqueous sodium carbonate but dissolves in acids, forming a yellow solution ; the colour is discharged by alkalis and regenerated by acids. The by-product, therefore, is very probably the lactonoid modification (annexed formula) of a pyrroylpyrrolecarboxylic acid,

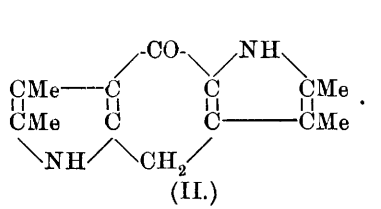




Tetramethylpyrrindoquinone is reduced to *tetramethylpyrrindole*-8-*ol* (formula I.) by zinc dust and glacial acetic acid under carefully regulated conditions, but when the reduction is effected slowly at the b. p., *tetramethylpyrrindolone* (formula II.) is formed.



I.)

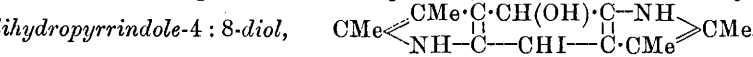


(II.)

Tetramethylpyrrindole-8-ol, pale brown crystals, m. p. about 358° (decomp.), darkening at about 300—330°, fluoresces faintly in alcoholic solution, readily combines with acids to form coloured salts of tetramethyldihydropyrrindole-4 : 8-diol (see below), and develops an intense violet red coloration with alcoholic ferric chloride and a little sulphuric acid, the solution ultimately becoming turbid and depositing tetramethylpyrrindoquinone. Tetramethylpyrrindole-8-one, small, pale brown prisms, m. p. about 340° (decomp.) with previous darkening, is insoluble in alcohol, does not develop a coloration with alcohol and sulphuric acid, and becomes nearly black after the further addition of ferric chloride and boiling, the product yielding tetramethylpyrrindoquinone when heated.

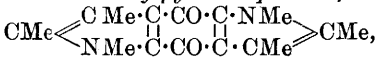
The reduction of tetramethylpyrrindoquinone by prolonged boiling with glacial acetic acid and hydriodic acid (D 1·97), yields several

products, of which only tetramethylpyrrindole-8-one has been identified. However, by heating on the water-bath for a few minutes with glacial acetic acid and a large excess of hydriodic acid, the characteristic reduction product is a *substance*, $C_{14}H_{17}ON_2I$, slender yellow needles, m. p. 255°, which is probably the *iodide* of *tetramethyldihydropyrrindole*-4 : 8-*diol*,



It readily oxidises and becomes superficially green in moist air, and changes in alcoholic solution to the pyrrindole-8-one or pyrrindole-8-ol. When it is boiled with absolute alcohol and copper powder, a deep blue, intensely fluorescent solution is obtained; the colour and fluorescence disappear when the solution is concentrated, and ultimately quite colourless crystals of tetramethylpyrrindole-8-ol are obtained. The intensely fluorescent substance is claimed to be tetramethyldihydropyrrindole-4 : 8-diol, the *sulphate*, yellow needles, and the iodide (preceding compound) are readily obtained from tetramethylpyrrindole-8-ol and the requisite acid. The iodide is converted into tetramethylpyrrindole-8-one by pyridine.

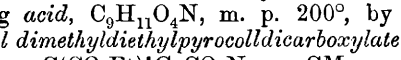
1 : 2 : 3-Trimethylpyrrole-4-carboxylic acid is converted by boiling acetic anhydride into *hexamethylpyrrindoquinone*,



orange-red prisms, m. p. 334° with partial sublimation, which is reduced by hot glacial acetic acid and zinc dust to *hexamethylpyrrindole*-8-*ol*, $C_{16}H_{20}ON_2$, m. p. 274°, and a colourless *substance*, m. p. 237°.

2 : 3-Dimethylpyrrole-4 : 5-dicarboxylic acid (Piloty and Wilke, *loc. cit.*) has m. p. 223·5°, and forms a *dipotassium* salt, six-sided, pearly plates. Attempts to produce a fluorescein from it have been unsuccessful. By heating the 4-ethyl hydrogen ester with hydrated oxalic acid at 105°, a dye, green metallic crusts, is produced which appears to be analogous to the dipyrrylmethylene dyes rather than to carbazole blue.

4-Ethyl hydrogen 2-methyl-3-ethylpyrrole-4 : 5-dicarboxylate (Piloty and Wilke, A., 1912, i, 899) is more readily obtained by using ethyl hydrogen oxalacetate instead of the diethyl ester. It is converted into the corresponding *acid*, $C_9H_{11}O_4N$, m. p. 200°, by hydrolysis with alkali, yields *ethyl dimethyldiethylpyrocolldicarboxylate*,



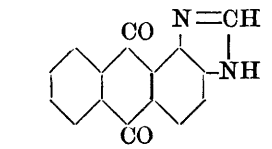
m. p. 159°, yellowish-white needles, by boiling with acetic anhydride, and is converted into *ethyl* 2-*methyl*-3-*ethylpyrrole*-4-*carboxylate*, $C_{10}H_{15}O_2N$, m. p. 108°, faintly rose-coloured needles, by heating at 210° in a current of carbon dioxide. 2-*Methyl*-3-*ethylpyrrole*-4-*carboxylic acid*, $C_8H_{11}O_2N$, almost colourless, rhombic plates, m. p. 128°, loses carbon dioxide by heating above its m. p. in a vacuum and yields 2-*methyl*-3-*ethylpyrrole*, $C_7H_{11}N$, b. p. 75—77°/15 mm. The *picrate* $C_{20}H_{25}O_7N_5$, orange-yellow, rhombic plates, m. p. 136°, prepared from the methylethylpyrrole, is a derivative of *bis*-2-*methyl*-3-*ethylpyrrole*,

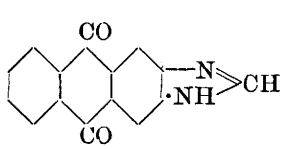
CMe<CEt·CH·CH·CEt / NH·CH·CH·NH>CMe, b. p. about 172°/15 mm., the hygroscopic *hydrochloride* of which is obtained by passing hydrogen chloride into a dry ethereal solution of 2-methyl-3-ethylpyrrole. By adding methyl sulphate to a boiling benzene solution of the potassium derivative of ethyl 2-methyl-3-ethylpyrrole-4-carboxylate and hydrolysing the product with methyl-alcoholic potassium hydroxide, 1 : 2-*dimethyl-3-ethylpyrrole*-4-*carboxylic acid*, $C_9H_{13}O_2N$, monoclinic needles, m. p. 210°, is obtained, which yields 1 : 2-*dimethyl*-3-*ethylpyrrole*, b. p. 59—61°/10 mm., by heating at 230° in a current of carbon dioxide.

By heating with acetic anhydride at 170°, 2-methyl- and 1 : 2-dimethyl-3-ethylpyrrole-4-carboxylic acids are converted respectively into *dimethyldiethylpyrrindoquinone*, CMe<CEt·C·CO·C·NH / NH·C·CO·C·CEt>CMe, brownish-red, microscopic prisms, subliming with partial decomposition, and *tetramethyldiethylpyrrindoquinone*, $C_{18}H_{22}O_2N_2$, red prismatic needles, m. p. 234°. The two quinones are reduced by zinc dust and boiling glacial acetic acid to *dimethyldiethylpyrrindole*-8-*ol*, $C_{16}H_{20}ON_2$, m. p. about 305—310°, and *tetramethyldiethylpyrrindole*-8-*ol*, $C_{18}H_{24}ON_2$, colourless rhombic plates, m. p. 194—200°. C. S.

Iminazoles of the Anthraquinone Series. ALFRED SCHAARSCHMIDT (*Annalen*, 1915, **407**, 176—194).—Various types of iminazoles of the anthraquinone series have been prepared by condensing 1 : 2- or 2 : 3-diaminoanthraquinone with anthraquinone-2-carboxylic acid or-2-aldehyde or with ω-dichloro-2-methylanthraquinone, in the presence of sulphuric or acetic acid. These condensations proceed quantitatively, but that with anthraquinone-1-carboxylic acid or its nitrile is much slower and incomplete.

Iminazoles of the types I and II, produced from the intensely coloured *o*-diaminoanthraquinones, are faintly yellow and do not yield vat dyes; on the contrary, the 2-phenyl derivatives are yellow and their vats dye cotton yellow.


(I).


(II.)

Vat dyes are also obtained from anthraquinoneiminazoles containing an anthraquinonyl group in position 2, excepting those in which the anthraquinonyl group has been produced from anthraquinone-1-carboxylic acid (or its nitrile).

The acid character of the anthraquinoneiminazoles increases rapidly with the molecular weight. Those of types I and II, but not the 2-phenyl derivatives, are soluble in dilute mineral acids; however, even iminazoles containing two anthraquinonyl groups yield, by solution in concentrated sulphuric acid and the careful addition of water, colourless sulphates which are hydrolysed by the addition of more water.

Anthraquinoneiminazoles are very resistant to reagents. Sodium hypochlorite or bromine water is without effect, and alkaline reducing agents only attack the carbonyl groups.

[With H. LEU.]—1 : 2- and 2 : 3-Diaminoanthraquinones are readily obtained by the following method. 2-Aminoanthraquinone and ethyl chlorocarbonate are heated together in boiling nitrobenzene and the resulting urethane is nitrated by sulphuric acid and nitric acid (D 1·4) in the cold. The mixture of 1- and 3-nitroanthraquinone-2-urethanes is isolated and separated into its constituents by crystallisation from nitrobenzene, the 3-nitro-compound being the less soluble. The substances are hydrolysed by dilute sulphuric acid, and the resulting 1- and 3-nitro-2-aminoanthraquinones are reduced by aqueous sodium sulphide.

α-Anthraquinoneiminazole (formula I.), faintly yellow crystals, m. p. above 300°, is prepared by boiling 1 : 2-diaminoanthraquinone with concentrated formic acid. *β-Anthraquinoneiminazole* (formula II.), prepared in a similar manner from 2 : 3-diaminoanthraquinone, forms yellow crystals, m. p. above 305°, and yields a hydrochloride and an orange-yellow *sodium* derivative.

2-*Phenyl-α-anthraquinoneiminazole*, $C_{21}H_{12}O_2N_2$, prepared by heating equal molecular quantities of 1 : 2-diaminoanthraquinone and benzoic acid with concentrated sulphuric acid at 150—160° or by boiling the diamine with benzoyl chloride, has m. p. 271° and forms a brownish-red vat producing on cotton orange-yellow shades changing to pure yellow by oxidation. 2-*Phenyl-β-anthraquinoneiminazole*, m. p. above 305°, is prepared in a similar manner and yields with alkaline hyposulphite a blue solution, in which cotton is dyed faintly yellow.

2(2′)-*Anthraquinonylbenziminazole*, $C_6H_4\langle\begin{matrix}-N\\NH\end{matrix}\rangle C\cdot C_6H_3\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_4$,

yellow crystals, m. p. above 300°, is prepared by heating to boiling a mixture of anthraquinone-2-aldehyde in glacial acetic acid and *o*-phenylenediamine in ethyl alcohol; its vat is brown and dyes cotton yellow. 2(2′)-*Anthraquinonyl-α-anthraquinoneiminazole*,

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_2\langle\begin{matrix}-N\\NH\end{matrix}\rangle C\cdot C_6H_3\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_4,$$

greenish-yellow, crystalline powder, m. p. above 300°, is prepared from anthraquinone-1-carboxylic acid and 1 : 2-diaminoanthraquinone in concentrated sulphuric acid at 160—170°; its vat is red and dyes cotton faintly yellow. 2(2′)-*Anthraquinonyl-β-anthraquinoneiminazole*, yellow crystals, m. p. above 300°, is prepared in a similar manner and its vat is similar to the preceding. Under the same conditions anthraquinone-1-nitrile and 2 : 3-diaminoanthraquinone yield the preceding iminazole, and anthraquinone-2-carboxylic acid and 1 : 2-diaminoanthraquinone yield 2(2′)-*anthraquinonyl-α-anthraquinoneiminazole*, yellow needles, m. p. above 310°, which forms an orange-red *sodium* derivative and a red vat.

By the preceding methods, 1 : 2-diaminoanthraquinone also yields 2(2′)-anthraquinonyl-α-anthraquinoneiminazole by treatment with anthraquinone-2-aldehyde or ω-dichloro-2-methylanthraquinone, whilst 2 : 3-diaminoanthraquinone yields 2(2′)-*anthraquinonyl-β-anthraquinoneiminazole*, yellow, crystalline powder, m. p. above 310°, by reaction with anthraquinone-2-aldehyde or 2-carboxylic acid or with ω-dichloro-2-methylanthraquinone. C. S.

s-Diaminotetrazine [3 : 6-Diamino-1 : 2 : 4 : 5-tetrazine]. IV. G. Ponzio and C. Gastaldi (*Gazzetta*, 1915, **45**, i, 181—183; compare A., 1913, i, 1109; 1914, i, 593).—When aminoguanidine hydrogen carbonate is heated, it loses carbon dioxide and water, yielding aminoguanidine, which then loses ammonia, giving rise to 3 : 6-diamino-1 : 2-dihydro-1 : 2 : 4 : 5-tetrazine. Under suitable experimental conditions, the latter undergoes oxidation, by means of atmospheric oxygen, to 3 : 6-diamino-1 : 2 : 4 : 5-tetrazine, which is, however, obtained in only small yield, since the bulk of the aminoguanidine remains unchanged.

Treatment in the cold of 3 : 6-diamino-1 : 2 : 4 : 5-tetrazine, in concentrated aqueous solution, with acids, yields the yellow, crystalline *hydrobromide*, which explodes with great violence at about 120°, the amorphous, yellow *picrate*, etc. The *hydrogen carbonate*,

$$C_2H_4N_6,H_2CO_3,$$

forms stable, orange-yellow plates, and at 100° loses carbon dioxide and water, giving the anhydrous base. T. H. P.

Purines. XVI. Isomeric Monomethyl Derivatives of 4-Amino-2-methylthiol-6-pyrimidone. 6 : 8-Dihydroxy-2-methylthiol-1-methylpurine. Carl O. Johns and Byron M. Hendrix (*J. Biol. Chem.*, 1915, **20**, 153—160).—On methylation of 4-amino-2-methylthiol-6-pyrimidone (A. 1913, i. 774) with methyl sulphate, two compounds are obtained, which can be separated by extraction with ether. The ether-soluble compound, *4-amino-6-methoxy-2-methylthiolpyrimidine*, sublimes if slowly heated at 90°, and has m. p. 144°. The same substance is obtained by the reduction of 6-chloro-4-amino-2-methylthiolpyrimidine with sodium methoxide, which indicates the structure of the compound. The ether-insoluble compound, which is the chief product, is *4-amino-2-methylthiol-1-methyl-6-pyrimidone*, m. p. 255°; prisms from alcohol. It is identical with a compound previously obtained from 4-amino-2-thio-6-pyrimidone and wrongly assumed to be 4-amino-6-methoxy-2-methylthiolpyrimidine (A., 1905, i, 836).

5-Nitroso-4-amino-2-methylthiol-1-methyl-6-pyrimidone is prepared by the action of nitrous acid on 4-amino-2-methylthiol-1-methyl-6-pyrimidone. It crystallises in blue prisms, m. p. 235°. Reduction of the nitroso-compounds with ammonium sulphide leads to the formation of *4 : 5-diamino-2-methylthiol-1-methyl-6-pyrimidone*, acicular prisms from water, m. p. 212°. The latter compound, when heated with carbamide at 160°, evolves ammonia and forms *6 : 8-dihydroxy-2-methylthiol-1-methylpurine*, which decomposes above 300° without melting.

H. W. B.

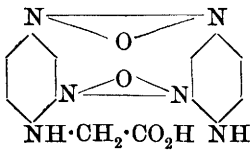
Conversion of 2 : 6-Dinitro-4-hydroxylaminotoluene into 2 : 6-Dinitro-4-azoxytoluene. R. Anschütz and Willy Zimmermann (*Ber.*, 1915, **48**, 152—156).—According to Cohen and Dakin (T., 1902, **81**, 27), the reduction of 2 : 4 : 6-trinitrotoluene by hydrogen sulphide gave 2 : 4-dinitro-6-hydroxylaminotoluene, which, when treated with concentrated hydrochloric acid, gave a product, m. p. 212—213°; this they regarded as 2 : 4-dinitro-6-aminotoluene. Later, Cohen and McCandish (T., 1905, **87**, 1205) showed the former substance to be

2 : 6-dinitro-4-hydroxylaminotoluene, which left the constitution of the latter unexplained. Repetition of the experiments has now shown that this substance is 2 : 6-dinitro-4-azoxytoluene.

Reduction of 2 : 4 : 6-trinitrotoluene in cold ammoniacal-alcoholic solution by hydrogen sulphide gives 2 : 4-dinitro-6-aminotoluene, m. p. 155°, and 2 : 6-dinitro-4-hydroxylaminotoluene, m. p. 135—136°. The latter is converted by boiling concentrated hydrochloric acid into 2 : 6-dinitro-4-aminotoluene, m. p. 168—169°, and 2 : 6-dinitro-4-azoxytoluene, m. p. 212—213°. The composition of the latter is deduced from analyses and determinations of molecular weight.

H. W.

2 : 4-Dinitrophenylglycine. EDM. WALDMANN (*J. pr. Chem.*, 1915, [ii], **91**, 190—202).—2 : 4-Dinitrophenylglycine is obtained in good yield by heating a mixture of glycine, sodium hydrogen carbonate, and chloro-2 : 4-dinitrobenzene in 65% alcoholic solution (compare Sanna, A., 1905, i, 48) and on reduction with stannous chloride in alcoholic solution is converted into 2 : 4-*diazoxyphenylglycine* (annexed formula) crystallising in lustrous, yellowish-brown leaflets, which become dark red at 217°, and decompose at a higher temperature; the *ethyl* ester, prepared by reducing the ethyl ester of 2 : 4-dinitrophenylglycine in a similar manner, forms glistening, dark red leaflets.



Reduction of 2 : 4-dinitrophenylglycine with tin and hydrochloric acid results in the formation of *7-amino-2-hydroxy-3 : 4-dihydroquinoxaline*, $NH_2 \cdot C_6H_3 \begin{cases} N{=}C \cdot OH \\ NH \cdot CH_2 \end{cases}$. This crystallises with $2H_2O$ in lustrous, yellow needles, which become orange at 155°, m. p. 181°; when kept, the crystals lose their lustre, acquire a green colour, and no longer dissolve in water.

The dihydroquinoxaline yields salts with both acids and alkalis; the *hydrochloride*, B,2HCl, forms white needles, m. p. above 300° (decomp.) with previous darkening; the *stannichloride*, long, white needles; the *sulphate*, B,H_2SO_4, separates from a solution of the dihydroquinoxaline in hot dilute sulphuric acid, in the form of pink, flattened needles, and on crystallisation from water is transformed into a *sulphate* of the composition $2C_8H_9ON_3,H_2SO_4$, crystallising in small, intensely red leaflets; the *oxalate*, $B,H_2C_2O_4$, forms red leaflets, which become white when heated, and melt at 219° to a ruby red liquid; the *ferrocyanide* crystallises in lustrous, silvery leaflets; the *potassium* salt, *sodium* salt, C_8H_8ONa,H_2O, small, yellow leaflets, and *triacetyl* derivative are also described. On treatment with sodium nitrite in hot acid solution, the hydrochloride is converted into *2 : 7-dihydroxy-3 : 4-dihydroquinoxaline*, $OH \cdot C_6H_3 \begin{cases} N{=}C \cdot OH \\ NH \cdot CH_2 \end{cases}$. This separates in a reddish-brown, floculent precipitate, which remains practically unchanged when heated at 305°, but in a moist condition becomes black and lustrous.

7-Amino-2 : 3-dihydroxyquinoxaline hydrochloride,

$$NH_2\cdot C_6H_3\!<\!\begin{matrix}N{:}C\cdot OH\\ |\\ N{:}C\cdot OH\end{matrix}\!>\!,HCl \quad \text{or} \quad NH_2\cdot C_6H_3\!<\!\begin{matrix}NH\cdot CO\\ |\\ NH\cdot CO\end{matrix}\!>\!,HCl$$

obtained by oxidising 7-amino-2-hydroxy-3 : 4-dihydroquinoxaline hydrochloride with ferric chloride in aqueous solution, forms a lustrous, brown, crystalline powder, possessing acid properties, and is not fused at 305°; oxidation with bromine water gives rise to a yellow, flocculent *dibromoaminodihydroxyquinoxaline*, $C_8H_5O_2N_3Br_2$, which remains unchanged when heated to 305°. F. B.

Azotisation by Chloroamine. Martin Onslow Forster (T., 1915, **107**, 260—267).—Experiments have been conducted with a view to ascertain the mechanism of azoimide formation from ammonia and diazonium perbromides. If the latter are really *N*-tribromohydrazines [a theory advanced by Chattaway (T., 1909, **95**, 862) and criticised by the author in the light of the experimental work of Hantzsch (A., 1896, i, 92) and of Bülow and Schmachtenberg (A., 1908, i, 743)], there appears to be no alternative to the cycloid structure for triazo-compounds. If, however, they are genuine perhaloids, two explanations are possible, one of which is as follows :

$$X\cdot\underset{\underset{\cdot\cdot}{N}}{N}\cdot Br,Br_2 + NH_3 = 3HBr + \left[\begin{matrix}X\cdot N\cdot N\\ \underset{\cdot\cdot}{N}\end{matrix}\right].$$

$$\left[\begin{matrix}X\cdot N\cdot N\\ \underset{\cdot\cdot}{N}\end{matrix}\right] \longrightarrow X\cdot N\!<\!\begin{matrix}N\\ ||\\ N\end{matrix} \text{ or } X\cdot N{:}N{:}N.$$

The alternative depends on the production of bromoamine, which, although existing only momentarily, might yield a diazoamino-compound of such a type that excess of ammonia would convert it immediately into the arylazoimide by loss of hydrogen bromide :

$$\underset{\underset{\cdot\cdot}{N}}{X\cdot N\cdot Br} + NH_2Br = X\cdot N{:}N\cdot NHBr + HBr.$$

$$X\cdot N{:}N\cdot NHBr - HBr = X\cdot N{:}N{:}N.$$

On account of its unstable nature, bromoamine itself cannot be used in this connexion, but it is shown that the diazonium group is transformed by chloroamine into the triazo-nucleus ; the yield is poor, but the reaction is definite and occurs under conditions in which hydrazine cannot be present in the solution.

The azotising action of chloroamine has been extended to the monoximes of *a*-diketones, to oximinocamphor and oximinoepicamphor ; it has not been found applicable to *p*-nitrosophenol or nitrosobenzene ; it therefore appears probable that, in alkaline solution, the former behaves as a true nitroso-compound rather than as the monoxime of *p*-benzoquinone.

Action of Chloroamine on Diazonium Salts.—The amine is diazotised, treated with sodium carbonate until faintly alkaline, and then with the calculated amount of sodium hypochlorite solution, which, immediately beforehand, has been mixed with ammonia. In this manner, aniline gives phenylazoimide in an impure condition. From -nitroaniline, however, *p*-nitrophenylazoimide, m. p. 72°, can be

isolated. To test for the possible presence of hydrazine, a solution of chloroamine similar to that used in the above experiments is shaken with benzaldehyde; separation of benzalazine does not occur, an oil being formed which is doubtless benzylidenechloroamine, Ph·CH:NCl (compare Cross, Bevan, and Bacon, T., 1910, **97**, 2404). Treatment of *p*-nitrobenzenediazonium chloride with sodium hypochlorite yields the diazoamino-compound; with diazotised aniline and *p*-bromoaniline a precipitate is formed which becomes tarry during filtration, so that the diazoamino-compound cannot be isolated in the crystalline form.

Action of Chloroamine on Oximinoketones.—*syn*-Oximinocamphor (m. p. 154°), when dissolved in normal sodium hydroxide and treated with chloroamine solution, yields diazocamphor, which is also obtained from *anti*-oximinocamphor, m. p. 114°. There appears to be no material difference between the behaviour of the two isomerides. Under suitable conditions, the Claisen mixture of the two isomerides can be made to give a 70 per cent. yield of diazocamphor.

The action of chloroamine on *syn*-oximinoepicamphor, m. p. 170°, gives a product, m. p. 111°, which is doubtless diazoepicamphor, and is being further investigated; with the anti-isomeride, m. p. 137°, an inferior yield of diazoepicamphor is produced, together with a colourless substance, m. p. 272°.

syn- and *anti*-Benziloximes give diazodeoxybenzoin and benzonitrile, the proportion of the latter being greater in the case of the anti-isomeride.

When a solution of chloroamine is added to piperidine and the product shaken with benzaldehyde, benzylidenepiperylhydrazone, lustrous plates, m. p. 68°, is formed. Knorr (A., 1884, 468) records 62—63°. H. W.

The Oxidising Power of Oxyhæmoglobin. J. F. McClendon (*Amer. J. Physiol.*, 1915, **36**, 366—367).—Some leuco-bases (e.g., aloin) are coloured by red corpuscles in the absence of hydrogen peroxide. Oxyhæmoglobin recrystallised 5 times, and methæmoglobin recrystallised 7 times, produce the same effect; it cannot therefore be due to oxydases. For the study of oxydases it is, therefore, necessary to remove all traces of blood-pigment. Lactic acid and sugars are not oxidised to carbon dioxide and water by oxyhæmoglobin, or by blood-charcoal. W. D. H.

Organic Phosphoric Acid Derivatives of Biochemical Importance. B. Sjollema (*Chem. Weekblad.*, 1915, **12**, 128—143).—A historical account of the development of knowledge regarding the constitution of the nucleoproteins and nucleic acids. A. J. W.

The Comparative Rate of Oxidation of Enzymes and their Pro-enzymes. W. E. Burge (*Amer. J. Physiol.*, 1915, **36**, 357).—Pepsinogen is more resistant to oxidation than pepsin, and trypsin is more easily oxidised than trypsinogen. W. D. H.

Influence of the Hydrogen Concentration on the Optimum Temperature of a Ferment. Arthur Compton (*Proc. Roy. Soc.*, 1915, [*B*], **88**, 408—417. Compare A., 1914, i, 1149).—The optimum

temperature for the activity of maltase varies with the degree of concentration of the hydrogen ions of the medium. H. W. B.

Amylases. VIII. Influence of Certain Acids and Salts on the Activity of Malt Amylase. H. C. SHERMAN and A. W. THOMAS (*J. Amer. Chem. Soc.*, 1915, **37**, 623—643).—The experiments described in this paper were carried out with purified malt amylase prepared by Sherman and Schlesinger's method (A., 1913, i, 1255). The effects of acetic, propionic, phosphoric, hydrochloric, nitric, and sulphuric acids, and of the chlorides, nitrates, sulphates, and dihydrogen phosphates of sodium and potassium, have been studied with reference to the determination of concentrations favouring optimum activity of the amylase. All these electrolytes increase the activity of malt amylase. The acids exert a greater activating influence than the normal salts, whilst the acid phosphates increase the saccharogenic activity to as great an extent as any of the acids. The weak acids, the strong acids, and the acid phosphates all showed optimum activation in those concentrations which have the same actual acidity; the optimum hydrogen ion concetration, expressed by Sörensen's exponent, was in each case between p_H^+ 4·2 and 4·6. When the acids are present in concentrations greater than the optimum, they produce a marked depression in the activity of the enzyme. Whether the activating agent be either an acid or a salt, the amyloclastic action reaches an optimum at a concentration of the electrolyte much below that which gives the optimum saccharogenic action. Concentrations which give the optimum saccharogenic activity are so much above the optimum for amyloclastic action as to show a distinct inhibitory influence. E. G.

Amylases. IX. Further Experiments on the Purification of Malt Amylase. H. C. SHERMAN and M. D. SCHLESINGER (*J. Amer. Chem. Soc.*, 1915, **37**, 643—648).—In continuation of their work on the purification of malt amylase (A., 1913, i, 1255), the authors have made amylase preparations of diastatic power ranging from 1200 to 2350 (Lintner's scale). The methods of purification were similar to those already described (*loc. cit.*). E. G.

Enzyme Action. XIII. Lipase of Soy Beans. K. GEORGE FALK (*J. Amer. Chem. Soc.*, 1915, **37**, 649—653).—The lipolytic activity of the enzymes of the soy bean has been studied by similar methods to those employed in the work on castor bean and duodenal lipases (A., 1912, i, 522: 1913, i, 303, 433, 664; 1914, i, 98, 759; this vol. i, 92).

It has been found that soy beans contain a lipase, active towards glyceryl triacetate, which is fairly soluble in water and has a maximum solubility in 1·5 *N*-sodium chloride solution. This enzyme has been compared with those of castor beans and the duodenal contents, and it is shown that the effects of neutral salt solutions and alcohol on the activity of all these lipases are very similar. The action of heat and of drying on the soy bean lipase resembles their action on the lipase and esterase of the castor bean. The results of

analyses of the soy bean lipase preparations did not differ greatly from those of the castor bean preparations. E. G.

A Starch-forming Enzyme from Malt. Its Action on Hemicelluloses and its Commercial Application to Brewing. CHARLES B. DAVIS (*J. Ind. Eng. Chem.*, 1915, **7**, 115—118).—An enzyme which is capable of converting hemicellulose into starch may be separated from malt by macerating the latter with water containing 1% of toluene for 4½ hours at 15·5° to 21°; the liquid portion is then separated, heated at 81° to destroy diastase, again filtered, cooled to 15·5°, and mixed with a large volume of alcohol. After 24 hours, the precipitate is collected, washed with alcohol and water (4 : 1), then dissolved in water, again precipitated with alcohol, collected, washed with alcohol and ether, and dried in a dessicator. This dry residue is extracted with water and the aqueous solution evaporated over sulphuric acid. The residue thus obtained is capable of converting 1000 times its weight of hemicelluloses into starch; the substance is not coagulated by boiling, is not precipitated by zinc sulphate, but is precipitated by phosphotungstic acid, metallic salts, alcohol, and tannin. At temperatures between 15° and 90°, it converts granulose, starch cellulose, amylocellulose, amylopectin, pentosans, and hexosans into gelatinised starch. The substance, for which the name "hemicellulase" is suggested, is of importance in brewing, particularly when refractory maize and rice products are employed. W. P. S.

Individuality of Oxidising and Reducing Enzymes. A. BACH (*Arch. Sci. Phys. nat.*, 1915, [iv], **39**, 59—71).—Woker (A., 1914, i, 603) has developed the theory that the different enzyme actions—peroxydase, catalase, oxygenase and perhydridase—are all due to the action of a single ferment having the properties of an aldehyde which acts differently according to the nature of the medium. A number of experimental facts are now brought forward to refute this hypothesis, and it is shown that each of the enzymes named has a clearly marked individuality.

Neither peroxydase, catalase, nor phenolase (that is, peroxydase + oxygenase) are able to reduce ammoniacal silver oxide in the cold, nor do they show a coloration with magenta-sulphurous acid. They have not therefore aldehydic properties. When boiled catalase solution, that is, the substances which accompany catalase and constitute its reaction medium, is added to purified peroxydase, the mixture is unable to liberate oxygen from hydrogen peroxide. In like manner, the addition of boiled peroxydase solution to catalase does not accelerate the oxidising action of hydrogen peroxide.

Peroxydase, together with a boiled phenolase solution, is not able to transfer molecular oxygen to oxidisable molecules. The enzyme mixture can only transfer oxygen feebly linked to peroxides to such oxidisable substances.

Even in presence of the substances which accompany perhydridase in milk together with acetaldehyde, peroxydase is unable to reduce nitrates. The appropriate medium has no effect in causing the enzyme to exercise a strange property. E. F. A.

Physiological Chemistry.

Apnœa. T. S. Githens and S. J. Meltzer (*Amer. J. Physiol.*, 1915, **36**, 363).—The cause of apnœa is not always chemical; it may occur without acapnia after a brief distension of the dog's lungs, even though the air used contains 5% of carbon dioxide; no such effect is obtainable after the two vagi are cut. W. D. H.

The Relation between the Red Corpuscles and Hæmoglobin to the Oxygen Tension of the Air. H. C. Dallwig, A. C. Kolls, and A. S. Loevenhart (*Amer. J. Physiol.*, 1915, **36**, 356—357).—A lowering of the oxygen tension below 14% atm. in the respired air increases the hæmoglobin and red corpuscles, and this is due to an increased activity of the bone marrow. The carbon dioxide tension is unimportant. The effect takes three to seven days to develop; the subsequent return to normal is slow, and may occupy two months. W. D. H.

Changes in Human Blood at High Altitudes. Edward C. Schneider and Leon C. Havens (*Amer. J. Physiol.*, 1915, **36**, 380—397).—The rapid increase in red corpuscles and hæmoglobin during the first few days at a great altitude is due in part to loss of fluid from the blood, and in part to the throwing into the circulation of reserve corpuscles. The blood-forming centres also become more active. Fatigue delays these phenomena. Physical exertion at sea-level, like abdominal massage, leads to increase of corpuscles and hæmoglobin, the reserve in the abdominal district being forced into the circulation. At high altitudes abdominal massage lowers the concentration of hæmoglobin and red corpuscles; the effect of physical exertion is also negligible until people become acclimatised after a stay of about six months; but even then the effect is a small one. W. D. H.

Oxidation in the Red Corpuscles of the Goose. J. F. McClendon (*Amer. J. Physiol.*, 1915, **36**, 364—365).—The oxidative colouring of leuco-bases by red corpuscles is increased by laking. Colorimetric methods for measuring intracellular oxidations were discarded since oxyhæmoglobin oxidises many of the substances used. The corpuscles were suspended in Ringer's solution, and shaken with air in a flask immersed in a thermostat, and connected to a water manometer. The oxygen absorbed was equal to the oxygen used by the cells since the hæmoglobin was saturated with oxygen at the start. Induction shocks do not increase intracellular oxidation, but strong shocks slightly increase electric conductivity, although no laking occurred. W. D. H.

The Coagulation of the Blood. L. Hirschfeld and R. Klinger (*Biochem. Zeitsch.*, 1915, **68**, 163—174).—Sodium soaps of certain fatty acids (especially oleic and erucic acids) act as cytozymes

in the manner attributed to such substances by Bordet and Delange. The properties are similar also to those of the natural cytozymes (from blood platelets and extracts of organs) in that they exhibit thermostability in pure solutions, but are thermolabile in the presence of serum, and are precipitated with the globulins. S. B. S.

The Diastases of the Blood. HUGH MCGUIGAN and C. L. VON HESS (*Amer. J. Physiol.*, 1915, **36**, 359—360).—The diastases of the blood do not dialyse though collodion. The injection of starch into the circulation increases the blood-sugar. This is attributed to enzymatic action in the blood. W. D. H.

The Sodium Chloride of the Plasma, and its Excretion in Normal and Diabetic Men. FRANKLIN C. MCLEAN (*Amer. J. Physiol.*, 1915, **36**, 357—358).—When the concentration of sodium chloride in the plasma falls below 0·56%, excretion ceases. Above this the rate of excretion varies as the square of the excess. In nine out of eighteen diabetic patients the same held; eight were excreting salt on a diminished threshold, and complained of "salt-hunger." In one case complicated with nephritis there was chloride retention. In one case complicated by dropsy, retention also occurred while the œdema lasted. W. D. H.

The Action of Serum and of Amino-acids on Urease. MARTIN JACOBY and N. UMEDA (*Biochem. Zeitsch.*, 1915, **68**, 23).—Rabbit's serum markedly increases the action of the Soja-bean urease. An active auxo-urease can also be isolated from sheep's serum, which can be obtained from the serum after separation of the proteins by heat coagulation in the presence of acetic acid, or by the extraction with water of the protein precipitate produced by the addition of alcohol. The substance thus obtained, unlike the native auxo-substance, is dialysable, and not destroyed by peptic digestion. Various amino-acids also increase the urease reaction, without being themselves acted on by the ferment. No difference was observed between the action of optically active and inactive acids. Asparagin, Witte's peptone, caseinogen, and glycyltryptophan also accelerate the urease action, but glutaric acid does not. Serum has but little action on the urease from *Robinia*. An auxo-substance is found also in calves' serum and human serum, and the infection of glycine only causes a minimal increase. S. B. S.

Influence of Salt-concentration on Hæmolysis. W. W. C. TOPLEY (*Proc. Roy. Soc.*, 1915, [*B*], **88**, 396—408).—In the case of the hæmolysis of the erythrocytes of the sheep by the complement in the serum of the guinea-pig, it is found that the presence of an excess of an electrolyte (sodium chloride) above the normal limit in a hæmolytic mixture prevents the combination of the complement with the erythrocyte–anti-substance complex. If the concentration of the anti-substance is markedly increased, it is possible, up to a certain point, to counteract the effect of the increased salt concentration. On the other hand, if the concentration of salt is

decreased below the normal, a decreased concentration of anti-substance suffices to produce the union of erythrocytes and complement. In an almost completely salt-free medium, the combination occurs in the complete absence of anti-substance. H. W. B.

Nitrogen Metabolism of a Man during Non-protein and Normal Diet after a Seven-day Fast. F. D. ZEMAN, J. KOHN, and PAUL E. HOWE (*Amer. J. Physiol.*, 1915, **36**, 362—363).—After the fast, a non-protein diet of the daily fuel value of 3500 cal. caused an increase of body-weight, due chiefly to retention of water and partly to that of the food stuffs given; the loss of nitrogen still continued, and even increased; some details of the various urinary constituents are given. When a normal diet was given normal conditions returned. W. D. H.

Metabolic Influences of Bathing in the Great Salt Lake. HELEN I. MATTILL and H. A. MATTILL (*Amer. J. Physiol.*, 1915, **36**, 488—500).—Bathing in the Great Salt Lake of two persons on a uniform diet stimulated nitrogenous metabolism, and caused a rise of 5 to 7% in the total nitrogen excreted. The elimination of creatinine rose slightly also, which may be due to increase of muscular tonus. The most remarkable result, however, was an increased secretion of chlorides (21—27%); the possibility of absorption through the skin is suggested and discussed.
W. D. H.

The Rate of Alcohol Resorption in the Organism of Animals in Cases where Tolerance has been Acquired and not Acquired, and on the Share of Alcohol in the Total Metabolism. WILHELM VÖLTZ and WALTER DIETRICH (*Biochem. Zeitsch.*, 1915, **68**, 118—139).—The organism of a dog, after an alcohol-free diet, contains volatile substances capable of reducing dichromate-sulphuric acid mixture in quantities equivalent to 0·12 c.c. alcohol per kilo. of body-weight. The rate of resorption of alcohol is appreciably greater in the case of animals that have acquired tolerance than in others. After doses of 2 c.c. alcohol per kilo. of body-weight ingested after a twenty-four-hours' fast, the following amounts were absorbed: In the case of an animal with acquired tolerance, 87·5% after one hour; in the case of an animal without tolerance, 66·2% after one hour, 95·8% after two hours. The oxidation of alcohol in the organism takes place slowly; the complete combustion under the conditions of experiment (2 c.c. alcohol per kilo. of body-weight, etc.), would require about eighteen hours; the difference in this respect in animals with and without tolerance is small. The alcohol oxidation formed in a ten-hour experiment is about 43%, and in a fifteen-hour experiment about 38% of the total energy exchange during a period of rest. S. B. S.

Utilisation of Calcium and Phosphoric Acid Compounds by the Animal Organism. III. Utilisation of the Chief Phosphoric Acid Compounds by Ruminants. GUSTAV FINGERLING (*Landw. Versuchs-Stat.*, 1915, **86**, 75—114).—Experiments with

lambs in which phosphorus was supplied in the forms of casein, phytin, lecithin, nuclein, sodium neucleate, and disodium phosphate. No essential differences in the results were observed, and the conclusion is drawn that the unsatisfactory results obtained with some foods cannot be due to the form of the phosphorus, but to the nature of the food itself. N. H. J. M.

Lipoids in Nutrition. C. G. MacArthur and C. L. Luckett (*J. Biol. Chem.*, 1915, **20**, 161—174).—The data presented indicate that lecithin, kephalin, cerebrosides, cholesterol, and fats are dispensable parts of a food for mice, but that a substance is present in egg-yolk, insoluble in ether, soluble in cold alcohol, and probably easily destroyed by heat, that needs to be added to a synthetic food (containing caseinogen, starch, lactose, lard, and milk salts) to make it a complete food. W. D. H.

Feeding Experiments on Rats. III. On Organs with an Internal Secretion. J. F. Gudernatch (*Amer. J. Physiol.*, 1915, **36**, 370—379).—Overdoses of thyroid produce the usual ill-effects; if the amount leads to no obvious ill-health, the rats do not breed, or if pregnancy ensues after the cessation of the thyroid feeding there may be abortion, early death of the offspring, or a diminution in their rate of growth. W. D. H.

Harmful Effect of a Vegetable Diet. Carl Voegtlin (*Amer. J. Physiol.*, 1915, **36**, 367).—Monkeys, mice, rats, pigs, and fowls were fed on an exclusively vegetable diet; they became ill, the central nervous system and alimentary canal being affected, and finally died. Fowls resist longest. Health is maintained by the addition of ox-liver, eggs, and milk; but extracts of liver and yeast exercised no protective influence; the addition of calcium and sodium phosphate prolongs life. W. D. H.

The Action of Glandular Extracts on the Secretion of Cerebro-spinal Fluid. Charles H. Frazier and M. M. Peet (*Amer. J. Physiol.*, 1915, **36**, 464—487).—Saline extracts of various organs and tissues (pancreas, spleen, kidney, liver, ovary, and testis) intravenously injected produce a slight, almost momentary, increase in the flow of cerebro-spinal fluid through a cannula placed in the fourth ventricle. This is not due to any increase in secretion, but is mechanically produced by turgidity of the cerebral venous sinuses (consequent on a fall in arterial pressure) forcing out fluid already present in the cerebral ventricles. The observations further confirm Dixon and Halliburton by finding that extracts of brain are the only animal extracts (other than that of the choroid gland itself) which cause a true increase in secretion. A new point brought out, however, is that extracts of the thyroid from dry or fresh preparations have an inhibitory effect on the secretory activity of the choroid gland. W. D. H.

Enzymes of the Central Nervous System. H. M. English and C. G. MacArthur (*J. Amer. Chem. Soc.*, 1915, **37**, 653—664).—An

account is given of a study of the enzymes of the brain. The results show that the brain contains a lipase, erepsin, an amylase, a catalase, enzymes which decompose arbutin and salol, and probably a pepsin or trypsin-like enzyme or both. The lipase is active towards glyceryl acetate and triacetate, and also acts on lecithin and kephalin. The activity increases directly with the amount of enzyme, the amount of the ester, and the time during which the enzyme is allowed to act. The activity is increased by the presence of sodium glycocholate, saponin, or a mixture of sodium mono- and di-hydrogen phosphates. The lipase is most active in a slightly acid medium, and the erepsin in an alkaline medium. In general, the grey matter is more active than the white. Extracts of the cerebrum, cerebellum, or mid-brain exhibit greater activity than those of the medulla or corpus callosum. Human brains and those of the ox, sheep, and dog all contain similar quantities of lipase. Neither peroxydase, oxydase, reductase, guanase, urease, nor rennin could be detected. E. G.

Metabolism in Nerve. SHIRO TASHIRO (*Amer. J. Physiol.*, 1915, **36**, 368—369).—The production of carbon dioxide in a nerve occurs in the direction of the nerve impulse; more of the gas is given off in nerves which conduct impulses rapidly. The temperature-coefficient is greater than occurs in physical processes. W. D. H.

Effects of Sodium Chloride on the Perfused Heart. W. BURRIDGE (*Quart. J. Expt. Physiol.*, 1915, 8, 303—330).—A displacement of calcium salts by sodium is a factor in producing diastolic failure in a frog's heart, when perfused with an isotonic solution of sodium chloride. After such perfusion, the action of calcium salts in shortening the refractory period, producing tonus, and supporting spontaneous contractions is increased. These changes are believed to be due to alterations in the state of aggregation of the heart colloids. W. D. H.

Action of Calcium Salts and Alkalis on the Perfused Heart. W. BURRIDGE (*Quart. J. Expt. Physiol.*, 1915, 8, 331—340).—Increased tonus follows the addition of traces of alkali to the perfusing solution; this is dependent on the calcium salts present, and is mediated by a change in the state of aggregation of the heart colloids. The effect of alkali in increasing the action of calcium is antagonised by calcium salts. The state of aggregation produced by calcium is thus unfavourable to its own activity. Alkalis first prolong and then shorten the refractory period. W. D. H.

The Lipoid Content of Vascular Endothelium. JOHN TAIT and JAMES A. HEWITT (*Quart. J. Expt. Physiol.*, 1915, 8, 391—394).—It is well known that blood-clotting is restrained by contact with the vascular lining. It is important to know if this is due to a greasy property of the endothelium, or to the amount of lipoid in

the endothelium of the aorta. The percentage of ether extract was about 9, a number not sufficiently high to warrant the conclusion that endothelium owes its properties to the amount of lipoid, although it is possible the lipoid may be accumulated towards the inner free surface. W. D. H.

The Lipoid Content of Peritoneal Endothelium. JOHN TAIT and WILLIAM CAMPBELL (*Quart. J. Expt. Physiol.*, 1915, **8**, 395—397).—The percentage of the ether extract in ox and sheep endothelium from the peritoneum is 13—15, nearly double that in the vascular endothelium. W. D. H.

Distribution of Gastrin in the Body. R. W. KEETON and F. C. KOCH (*Amer. J. Physiol.*, 1915, **36**, 353).—Gastrin was prepared from extracts of tissue made with 0·4% hydrochloric acid; the preparation was injected intramuscularly in dogs with gastric fistulæ. Gastrin is uniformly distributed over the stomach membrane, except in the cardiac region, where less active extracts were obtained; it is found slightly in the duodenum, and traces even occur in the œsophagus. Extracts of other tissues were inactive. W. D. H.

Action of Drugs on the Isolated Small Intestine. ALEXANDER W. YOUNG (*Quart. J. Expt. Physiol.*, 1915, **8**, 347—376).—Sodium hydrogen carbonate (0·01 to 0·04%) in Ringer's solution increases intestinal tonus, and does not affect the pendulum movements; stronger solutions inhibit movements. Hydrochloric acid (0·0005%) inhibits tone and movement. Carbon dioxide has the same effect. Hyoscyamine and hyoscine (less powerfully) stimulate movements, but inhibit the stimulation caused by pilocarpine. Cocaine when dilute stimulates, but 0·2% causes paralysis. Neurine and choline (less powerfully) raise the tonus, but obliterate movements; they are antagonised by atropine. Strong aqueous extracts of the posterior lobe of the pituitary increase tonus and develop large tonus oscillations. Adrenaline inhibits movements and tone; 1 in 10,000,000 causes a distinct effect. Extracts of spleen, thyroid, thymus, pancreas, liver, kidney, and brain gave no definite results. The stomach contents inhibit movements because of their acidity; the contents of the small intestine stimulate, but this is influenced by their reaction. Extracts of the digesting mucous membrane of stomach and small intestine, and also secretin, have, when neutral, no definite action. Pancreatic juice increases the tone. Indole and bile lower the tone and inhibit movements. W. D. H.

Mode of Action of Pituitary Extract on the Mammary Gland. SUTHERLAND SIMPSON and REUBEN L. HILL (*Quart. J. Expt. Physiol.*, 1915, **8**, 377—379).—The flow of milk in dogs (two experiments) which follows the injection of pituitary extract is due to an action on the secretory cells, not on the muscular tissue, since barium chloride, a specific stimulant of muscle, causes no milk to flow. Pituitrin causes its effect after the injection of barium chloride. W. D. H.

Mode of Action of Pituitary Extract on the Mammary Gland. E. A. SCHÄFER (*Quart. J. Expt. Physiol.*, 1915. **8**, 379—382). —A criticism of the preceding paper. The microscopic examination of full mammary glands, and those emptied after a dose of pituitrin, indicate that the act of discharge is produced by the contraction of the smooth muscle in the walls of the alveoli. A second injection after emptying does not yield a drop of milk until time elapses for the accumulation of more secretion. The assumption made by Simpson and Hill that barium chloride invariably produces contraction of every muscle cell in the body has never been proved. On the other hand, pituitrin is known to act powerfully on most, if not all, plain muscles. W. D. H.

The Action of Pituitrin on the Mammary Gland. W. L. GAINES (*Amer. J. Physiol.*, 1915, **36**, 360—361).—The experiments recorded on the goat confirm Schäfer's view that pituitrin acts on the musculature of the gland. W. D. H.

The Effect of Sodium Sulphate on the Submaxillary Gland. J. BARCROFT (*Proc. Physiol. Soc.*, 1915 ; *J. Physiol.*, **49**, xiv—xv).—Doses of sodium sulphate which cause diuresis, and increase the oxygen consumption of the kidney, have no such effect on the submaxillary gland. In some cases the oxygen used was lessened, suggesting that the salt is here a metabolic depressant. W. D. H.

The Sugar-forming Capacity of Normal and Fatty-degenerated Frog's Liver. VITTORIO SCAFFIDI (*Biochem. Zeitsch.*, 1915, **68**, 320—336).—The isolated frog's liver can form sugar from the glycogen it contains. Owing to the absence of glycogen in the fatty-degenerated liver, no sugar is formed, owing to the absence of the necessary material for its production, and not to the absence of a ferment, for if glycogen is added to the fatty degenerated liver, it is capable of forming sugar; and hydrolysis of the polysaccharide takes place just as it does in the normal liver. The absence of glycogen in the fatty-degenerated liver is thus confirmed, and this is due, not to a condition of starvation, but to the toxic action of the phosphorus employed to induce the degeneration. The intoxication does not, however, destroy the capacity of the liver to hydrolyse added glycogen. S. B. S.

The Size and Composition of the Thymus Gland. FREDERIC FENGER (*J. Biol. Chem.*, 1915, **20**, 115—118).—The proportional weight of the thymus is greater in fœtal and growing animals than in adults; the amount of blood, nuclein, and phosphates in the fœtal thymus indicates that it is active at least three months before birth. In full-grown animals the thymus also contains nuclein and phosphates, indicating that it does not cease acting during the reproduction period of these animals. Cattle and sheep contain more thymus tissue per body-weight than dogs. W. D. H.

The Influence of a Diet of Marine Algæ on the Iodine Content of Sheep's Thyroid. ANDREW HUNTER and SUTHERLAND SIMPSON (*J. Biol. Chem.*, 1915, **20**, 119—122).—The analyses show a very high percentage of iodine, and this result confirms the view that the amount of iodine in the thyroid is in part determined by the amount in the food. W. D. H.

The Effect of Partial Adrenal Deficiency on Sympathetic Irritability. R. G. HOSKINS (*Amer. J. Physiol.*, 1915, **36**, 423—429).—From one-half to seven-tenths of the adrenal tissue was removed in dogs. This caused a decrease in the reaction (of blood-pressure and vasomotor changes) to nicotine, but the reaction to adrenaline was not affected. The depression of the irritability of the sympathetic nervous system is probably only a part of a generalised interference with fundamental metabolism. W. D. H.

The Alleged Influence of Adrenaline and of the Sympathetic Nervous System on the Tissues of Skeletal Muscle. YAS KUNO (*J. Physiol.*, 1915, **49**, 139—146).—Section of the rami communicantes and administration of adrenaline (6:100,000) have no effect on the tonus of frog's muscle. W. D. H.

The Transformation of Energy in Muscle. JACOB PARNAS (*Proc. Physiol. Soc.*, 1914; *J. Physiol.*, **49**, vii—viii).—The conclusions drawn from the experiments described are: (1) the lactic acid due to muscular fatigue is completely burnt in the muscle, and not rebuilt into its substance; (2) about a half of the energy so liberated is stored as potential in the muscle; (3) no substances intermediate between lactic acid and carbon dioxide were found; (4) in crushed muscle the oxygen used is insignificant. W. D. H.

The Reactions of Resting and Active Muscles of the Frog. HEINRICH PECHSTEIN (*Biochem. Zeitsch.*, 1915, **68**, 140—162).—The $[H^{\cdot}]$ concentration was measured electrometrically of extracts of muscles, which had been rapidly killed after the various experiments by immersion in boiling water. The average value of p for resting muscles of summer frogs was 7·43 and for exhausted muscles 6·84. There is little difference in the reactions of the exhausted muscles, whether the circulation of the blood is left intact or not. The $[H^{\cdot}]$ concentration diminishes with the recovery of the muscles, and here, again, the influence of the blood circulation is small. S. B. S.

Bitches' Milk. W. GRIMMER (*Biochem. Zeitsch.*, 1915, **68**, 311—319; *Milch. Zentr.*, 1915, **44**, 34—40).—Of the proteins of the milk the caseinogen forms from 50—67%, the albumin 15—25%, and the globulin 15—25%. S. B. S.

Condition of Caseinogen and Salts in Milk. LUCIUS L. VAN SLYKE and ALFRED W. BOSWORTH (*J. Biol. Chem.*, 1915, **20**, 135—152).—The substances in solution can be separated from those

in suspension by filtering through a Pasteur-Chamberland filter. The following are in solution in the milk-serum: sugar, citric acid, potassium, sodium, and chlorine. The following are partly in solution, partly in suspension: albumin, inorganic phosphates, calcium, magnesium. In fresh milk the albumin is adsorbed to a large extent by caseinogen, but in some milk it nearly all appears in the serum. The material left by milk on the filter goes into suspension with water, and is neutral to phenolphthalein. It consists of neutral calcium caseinogenate and calcium hydrogen phosphate; these are not combined, and after treating fresh milk with formaldehyde, a nearly complete separation can be effected by the centrifuge. Fresh milk and its serum are slightly acid to phenolphthalein, but strongly alkaline to methyl-orange; the acidity is due in part, therefore, to acid phosphates. W. D. H.

The Secretion of Urine in Decerebrate Animals. J. Barcroft and H. Piper (*Proc. physiol. Soc.*, 1915; *J. Physiol.*, **49**, xiii—xiv).—Intravenous injection of Ringer's solution caused diuresis without increase in the oxygen consumption of the kidney, and the deduction was drawn that the urine was formed by physical causes, and not by increase of kidney work. These experiments by Barcroft and Straub (A., 1910, ii, 1090) were performed under urethane anæsthesia, and have been objected to on that score. The present experiments on decerebrate rabbits were therefore undertaken, and the results confirm those alluded to above.

W. D. H.

Hyperglycæmia produced by Adrenaline and by Anæsthesia. J. H. Burn (*Proc. physiol. Soc.*, 1915; *J. Physiol.*, **49**, xii—xiii).—Hyperglycæmia and glycosuria produced by adrenaline are prevented by injection of ergotoxine; hyperglycæmia produced by anæsthetics is not affected by ergotoxine, or by extirpation of the adrenal glands. It is therefore not due to increased output of adrenaline. Pituitary extract acts like ergotoxine in adrenaline hyperglycæmia, but extracts of thyroid and testis have no effect. Pituitary extract abolishes anæsthetic hyperglycæmia in rabbits, but not in cats; the effect on rabbits is attributed to direct deterrent action on glycogenolysis in the liver cells. W. D. H.

The Influence of Depancreatisation on the Glycæmia following the Intravenous Injection of Dextrose in Dogs. I. S. Kleiner and S. J. Meltzer (*Amer. J. Physiol.*, 1915, **36**, 360—362).—In normal dogs the blood-sugar content falls to the normal ninety minutes after an injection of dextrose; in depancreatised dogs the percentage at the end of this time may be twice the normal. The same is observed after removal of the kidneys.

W. D. H.

Theory of Diabetes. IV. Parallelism between the Effects of the Pancreas and those of Metallic Hydroxides on Sugars. R. T. Woodyatt (*J. Biol. Chem.*, 1915, **20**, 129—133).—A theoretical

paper in which it is suggested that the internal secretion of the pancreas brings about the breaking down of dextrose in the body in a similar way to that in which it is destroyed in vitro by strong alkali in the presence of metallic hydroxides. H. W. B.

The Cholesterol Metabolism in a Case of Congenital Hæmolytic Jaundice with Enlarged Spleen. JAMES P. MCKELVIE and JACOB ROSENBLOOM (*Biochem. Zeitsch.*, 1915, **68**, 78—84).—The authors confirm the observations of others as to the lessened resistance of the blood-corpuscles to hypotonic salt solutions. Metabolism experiments on the patient on a diet of known cholesterol content indicated a negative balance as regards this substance. As it is known to inhibit hæmolysis by various agents, the view is advanced that the patient is unable normally to degrade cholesterol, and this leads to a vicious circle, as the absence of the substance in blood causes hæmolysis, which is the reason of an increased amount of cholesterol circulating in the organism which is not held back by the serum. S. B. S.

The Rôle of Fluorine in the Animal Organism. G. B. VAN KAMPEN (*Chem. Weekblad*, 1915, **12**, 225—232).—A review of the work of Gautier and Clausmann on the physiological effects of fluorides. A. J. W.

Physiological Properties of Electrolytes. C. BONGIOVANNI (*Boll. Chim. Farm.*, 1915, **54**, 65—68).—Comparison of the physiological action of a compound in the ionised state with that which it exerts when not dissociated, that is, when in presence of a marked excess of a salt with a common ion, is admissible only when no complex salt is formed between the two compounds. Thus, Sabbatani's conclusions with reference to the toxicity of mercury ions (A., 1908, ii, 718) are invalidated owing to the formation, by mercuric chloride in presence of a large excess of sodium chloride, of a double salt of the type Na_2HgCl_4 or $NaHgCl_3$. Criticism is also advanced against Bottazzi's statements with reference to the toxicity and antiseptic action of mercuric chloride and silver nitrate dissolved in absolute alcohol (*Principii di Fisiologia*, 239) and against the observation made by Zanda (*Giorn. R. Accad. Torino*, 1913, **9**) and by Loew (*Science*, 1903, **18**, 305) that the corrosive action of hydrochloric acid is diminished when it is injected together with a large proportion of sodium chloride. The author is of opinion that only in a few special cases of local physiological action can the theory of electrolytic dissociation be applied with advantage. T. H. P.

Anæsthesia by Phenylethylmalonylcarbamide. W. L. SYMES (*J. Physiol.*, 1915, **49**, 126—132).—This substance, also known as "luminal," causes anæsthesia in cats when a dose of 0·2 gram is injected under the skin; the anæsthesia is usually complete in an hour, and lasts three to five hours. Smaller doses administered subcutaneously or by the mouth may be given overnight, and the

animal would be ready for an operation in the morning. Under the influence of the drug, the cat becomes poikilothermic. Cats may with care be kept unconscious for days, and then make a complete recovery; in rabbits intravenous injection may be used; anæsthesia is then rapidly produced. W. D. H.

Distribution of Mercury in the Body of a Case of Acute Mercuric Chloride Poisoning. JACOB ROSENBLOOM (*J. Biol. Chem.*, 1915, **20**, 123—124).—The various organs from a case of suicide were analysed by Ludwig's method; the liver contained the highest percentage amount, but the blood contained the largest absolute amount of mercury. W. D. H.

The Toxicity of Oil of Chenopodium. WILLIAM SALANT and E. K. NELSON (*Amer. J. Physiol.*, 1915, **36**, 440—463).—Chenopodium is about 30% less toxic than ascaridole, but the fatal dose varies in the animals used (dogs, cats, rabbits, and guinea pigs), being smallest for the cat. The symptoms (depression of the higher nerve-centres, then convulsions) vary somewhat also with the animal. The toxicity of chenopodium oil is increased in starvation and decreased by a diet rich in fats or carbohydrates. Detoxication by glycuronic acid derived from glycogen and glycerides is suggested. The suppression of symptoms by fixed oils may be explained by its solubility in oils. Cumulative effects were observed. W. D. H.

Chemistry of Vegetable Physiology and Agriculture

Favourable Action of Manganese on the Bacteria of Leguminoseæ. D. Olaru (*Compt. rend.*, 1915, **160**, 280—283).—The author has tried the effect of adding varying small quantities of manganese in the form of its sulphate to cultures of nodule bacteria, the medium being a decoction of haricot beans to which sugar had been added. In one series of experiments the maximum effect as measured by nitrogen fixation in forty-eight days was obtained by the addition of 1 part of manganese to 200,000 of medium. In two other series allowed to go respectively fifty and one hundred and fourteen days, the maximum effect was obtained in both cases by the addition of 1 part of manganese to 50,000 of medium. The nitrogen fixed was in one case 38·4% and in the other case 31·2% of the nitrogen originally present and 1·70% and 1·37% of the sugar originally present. In nearly every case only traces of sugar could be found in the culture solutions at the end of the experiment. W. G.

The Action of Rare Earths on Bacteria. A. Simonini (*Centr. Bakt. Par.*, 1915, i, **75**, 398—407).—Treatment of certain bacteria

with solutions of thorium salts results not only in changes in the morphology and staining reactions of the organisms, but their physiological characters are also affected. This includes a reduction of the specific toxicity of the organism without affecting its antigen functions. Exposure to the action of a 2% solution of thorium ammonium nitrate for one to three days is said to modify dysentery bacteria of the Shiga-Kruse and Flexner types and also *B. diphtheriae* to a marked degree, whilst *B. coli* shows less response. H. B. H.

Influence of the Character of the Soil on Bacteria and the Changes in the Soil. HARALD R. CHRISTENSEN (*Centr. Bakt. Par.*, 1915, ii, **43**, 1—166).—The results of inoculation experiments with a large number of soils showed that *Azotobacter* occurs very frequently in soils which contain sufficient calcium carbonate to effervesce when treated with hydrochloric acid; neutral soils seldom contain *Azotobacter*, whilst in acid soils it very rarely occurs.

As regards phosphoric acid, it is considered probable that a vigorous growth of *Azotobacter* in a mannitol solution free from phosphates is a certain indication that the soil is not deficient in phosphoric acid.

Microbes which ferment mannitol occur in practically all arable soils, in numbers which seem to depend mainly on the amount of calcium, in a suitable form, in the soil.

As regards the power of soils to decompose peptone, it is shown that great variations occur in different arable soils, depending partly on the composition (phosphoric acid being especially important), and partly on biological conditions. Addition of calcium carbonate was generally without effect, and none of the soils was influenced by addition of humus. A low power of decomposing peptone indicates unfavourable conditions for the growth of plants.

The rate of decomposition of cellulose in soils seems to depend on chemical conditions, since inoculation was without effect. Basic calcium and phosphoric acid are the chief factors.

It was previously shown that peat of the "Hochmoor" variety usually fails to produce nitrites in the solutions employed. This is shown to be due to the absence of nitrite organisms, and not to the presence of inhibiting substances. N. H. J. M.

Effect of Some Organic Soil Constituents on Nitrogen Fixation. HOWARD S. REED and BRUCE WILLIAMS (*Centr. Bakt. Par.*, 1915, ii, **43**, 166—176).—As regards the fixation of nitrogen by *Azotobacter* on sand with mineral nutrients and various non-nitrogenous organic compounds, it was found that with the exception of æsculin, quinic acid, and borneol, which increased the activity of *Azotobacter*, all the compounds employed caused a depression. Quinol and salicylaldehyde completely inhibited nitrogen fixation; most of the other compounds were, however, much less injurious than would be expected from their action on higher plants.

Many of the nitrogenous compounds employed, which have been found to be assimilated by higher plants, had a depressing effect on fixation, the simpler compounds having a more marked depressing effect than the more complex compounds. It is considered possible that the simpler compounds (carbamide, glycine, and formamide) are not toxic, but that their nitrogen is possibly utilised by *Azotobacter* in preference to elementary nitrogen. N. H. J. M.

Production of Enzymes and its Cause. Heinrich Zikes (*Biol. Zentr.*, 1915, **44**, 68—69; from *Monatsh. Landw.*, 1914, **7**, 24).—Yeast which had been cultivated for fourteen years in dextrose solutions at once fermented sucrose when transferred to sucrose solutions. Similar results were obtained with maltose solutions. The yeast still contained, therefore, both invertase and maltase in the form of a zymogen, after being cultivated for a number of years in dextrose solutions. N. H. J. M.

Phytochemical Reductions. V. The Intermediary Stages in the Reduction of the Nitro-groups to Amino-groups. C. Neuberg and E. Welde (*Biochem. Zeitsch.*, 1914, **67**, 18—23).—It has been already shown (A., 1914, i, 635) that nitrobenzene is reduced to aniline when added to a sugar-fermentation mixture. The experiments were carried out with the object of ascertaining which intermediary products were formed. It was found that when azoxybenzene or azobenzene is added to a fermentation mixture, little if any aniline was formed. On the other hand, from 21 grams of nitrosobenzene 4·0 grams of aniline were obtained, and from the same quantity of phenylhydroxylamine, 7·5 grams. In both cases azobenzene was also formed. The results appear to indicate that the intermediate products in the reduction of nitrobenzene to aniline are nitrosobenzene and phenylhydroxylamine. The bearing of these results on the reduction of nitrates by plants is discussed. S. B. S.

Phytochemical Reductions. VI. The Formation of *n*-Hexyl Alcohol by Yeast. C. Neuberg and F. F. Nord (*Biochem. Zeitsch.*, 1914, **67**, 24—27).—Whereas the aldehydes containing three, four, or five carbon atoms are readily reduced to the corresponding alcohols when added to a yeast fermentation mixture, a considerable resistance is offered to reduction by the 7-carbon atom aldehyde, heptaldehyde. It is now shown that the 6-carbon atom aldehyde, *n*-hexaldehyde, occupies an intermediate position, being reduced with greater difficulty than the lower aldehydes, but offering less resistance than the higher one. The addition of the aldehyde stops fermentation after a period, before the sugar is all destroyed, but the addition of fresh yeast causes the fermentation to start again. S. B. S.

Degradation of Wood by Fungi. C. Wehmer (*Ber.*, 1915, **48**, 130—134).—The author has investigated the decomposition (dry-rot) of wood by certain fungi, such as *Merulius lacrymans*, *Meru-*

lius silvester, *Comophora cerebella*, and *Polyporus vaporarius*. In a specimen of well-rotted pine, it is found that 100 parts of wood (51% C.) yielded 50 parts of carbon dioxide and water (and ferment matter), 7·5 parts of substance soluble in water (46—51% C.) consisting of a brownish-black, shining varnish or a coal-like, dull powder, 17·5 parts of matter soluble in alkali (64% C.) composed of shiny, blackish-brown particles, and 25 parts of insoluble turf-like residue (60% C.) composed of compact, brown masses showing the almost unchanged structure of wood under the microscope.

The amorphous matters isolatable from rotten wood form a series with successively decreasing oxygen content (and strongly increasing carbon content); the humus soluble in water contains relatively more oxygen than the original wood.

It has not yet been possible to determine the exact substance which is attacked by the fungi, but experiments on the action of the latter on pure cellulose are in progress. Sugars are readily attacked by *Merulius*, and the unused portions remain as humus.

The "acidity" of rotton wood is due to the presence of humus, free organic acids being absent. This acidity can be neutralised by alkali, but is restored by boiling with water, the rotten woody fibre merely absorbing the alkali superficially. H. W.

Free Nitrogen and the Higher Plants. Marin Molliard (*Compt. rend.*, 1915. **160**, 310—313).—Cultures were made of radish plants under aseptic conditions in solutions containing 0·25 gram of magnesium sulphate, 0·50 gram of ammonium chloride, 0·25 gram of potassium chloride, 0·25 gram of calcium phosphate, traces of ferrous sulphate, and 50 grams of dextrose per litre, the plants growing in an atmosphere free from ammonia and nitric acid. The results show that, after seven weeks' growth, within the limits of error, there is no fixation of nitrogen by this plant (compare Mameli and Pollacci, A., 1911, ii, 759). W. G.

Dissolving Action of Roots. Th. W. Tchirikov (*Bid. Zentr.*, 1915, **44**, 66—67; from *J. Exper. Landw.*, 1914, 64).—Experiments with barley and buckwheat manured with phosphorite are described.

Barley assimilates the phosphorus of phosphorite when isolated, but fails to assimilate it in presence of calcium nitrate or other calcium salts. Buckwheat assimilates phosphorite both in presence and in absence of calcium salts.

The conclusion is drawn that buckwheat takes up calcium more rapidly than phosphorus, and in this manner increases the solvent action of the soil water on the phosphoric acid of the phosphorite. In the case of barley, phosphorus is more rapidly removed from the soil solution than calcium. N. H. J. M.

The Later Researches on Anthocyanin. P. Q. Keegan (*Chem. News*, 1915, **111**, 87—88).—Grafe's opinion that a special chromogen

of anthocyanin does not exist, and that the pigment does not result from the simple oxidation of pre-existing substances is incorrect, in particular because in numerous cases the tannins of plants by suitable treatment assume a tint in solution absolutely comparable with that of the petals in their natural condition, and conclusive evidence exists to prove that the protoplasm which produces habitually a certain kind of tannin cannot produce any kind of pigment in the corolla. Plants producing phloroglucinol tannins yield original reds only, and those producing caffeotannins original blues, the chromogenic activity of the latter being much milder than that of those of the phloroglucinol type. There is only one anthocyanin pigment in plants of the latter type, the red on stems or petals being due to acid only. Yellow flowers are due to carotin or xanthophyll, and very rarely to a flavone. The white flower often encloses a very dilute solution of anthocyanin, but the absence of colour is due chiefly to the circumstance that intense deassimilation has not been occasioned in the corolla because the nitrogen needed by the reproductive organs has been fully supplied from other sources. G. F. M.

The Pigments of the Chromoleucites. V. LUBIMENKO (*Compt. rend.*, 1915, **160**, 277—280. Compare A., 1914, i, 468).—The author finds that the pigments contained in the chromoleucites can be divided into two groups: (1) the carottinoids insoluble in strong formic acid, (2) the xanthophylloids dissolving more or less easily in this acid giving green solutions. They both represent a series of substances intermediate between carrottin and xanthophyll, and may be considered as arising from the former by successive oxidation and from the latter by successive reduction. The chemical evolution of the pigments contained in the chloroleucites in the course of their transformation into chromoleucites consists in the formation of a large number of coloured substances, allied to carrottin, xanthophyll, and their two isomerides, lycopine and rhodoxanthin. The appearance of these intermediate substances together with lycopine and rhodoxanthin must be attributed to the two opposed chemical processes of oxidation and reduction, which replace one another during the development of the chlorophyll tissue, and which attack the apparatus of assimilation. During the period of active assimilation these two processes probably counterbalance one another, giving an apparent stability to the chlorophyll and the yellow pigments which accompany it. W. G.

Physiology of the Intake of Material by the Living Plant-Cell. III. Influence of Neutral Salts and some Non-electrolytes on the Toxic Action of Alcohols on Plant Cells. HELENE NOTHMANN-ZUCKERKANDL (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **2**, 19—41).—The exosmosis occurring when leaves of plants (*Echeveria, Saxifraga sarmentosa*, and *Tradescantia discolor*) are immersed in aqueous solutions of the lower alcohols increases if

neutral salts are also added. Those salts which, in aqueous solution, produce the greatest exosmosis have the greatest supplementary action on the osmosis caused by the alcohol solutions. It is probable that the observed augmentation on the addition of a salt is not due to an altered solubility of the alcohol, but to a summation of the separate actions of the two substances, alcohol and salt.

In the presence of butyl and higher alcohols, salts react usually in such a way as to reduce the exosmotic effect; but sometimes the action is so slight in comparison with the toxicity of the added salt that it is unobservable. The antagonism between butyl alcohol and salts is explained by the assumption that they enter the cell by the same path, and when both are present, each obstructs the passage of the other. Plasmolysis experiments, showing that the concentration limit of van't Hoff's solution which just produces plasmolysis is lowered by butyl alcohol, confirm this view. The author draws the conclusion that the hydrocolloids of the plasma must constitute the only path by which materials enter the plant-cell.

Tannic and aspartic acids and peptone increase the action of the various alcohols, whilst glycine, tyrosine, sucrose, and maltose are inactive. The osmotic power of non-electrolytes, as well as of salts, is therefore of secondary importance to the lyotropic influence in producing effects on plant-cells. H. W. B.

Chicory. V. Grafe (*Biochem. Zeitsch.*, 1915, **68**, 1—22).—The inulin-content of the roots depends on the water-content of the soil on which the plant is grown, being low when the plant is grown on wet soils. The ash-content varies between 5 and 6%, but the amount of "crude fibre" diminishes in plants from sand and loams, and increases on humus-rich soils. The amounts of inulin and bitter principles obtained from plants grown on loams and sands is also generally larger than those of plants from humus-rich soils. The bitter principle, the method of preparation of which is described, has not been obtained in a pure condition; it appears to be a glucoside of lævulose, and a protocatechuic derivative, probably the aldehyde, the former of which is derived from inulin, and the latter from the dextrin-like degradation products of the same. The empyreumatic oil obtained by roasting is analogous to the coffee-oil, and the chief constituent is acetic acid; it also contains valeric acid and acraldehyde and furfuryl alcohol (23—25%). S. B. S.

The Active Principles of Rice Husks. H. Kondo and N. Gomi (*J. Pharm. Chim.*, 1915, [vii], **11**, 37—38; from *Yakugakuzasshi*, 1914).—Rice husks and the extract prepared therefrom with 90% alcohol have a curative effect on pigeons suffering from beri-beri induced by a diet of shelled rice; an extract prepared with 20% alcohol is less active. Oryzanin, prepared by the process described by Suzuki (A., 1912, ii, 980), does not possess any curative proper-

ties. Oryzanin appears to consist of a mixture of substances, the authors having separated from it choline, nicotinic acid, adenine, and a substance having the nature of a glucoside; they have also detected the presence of sucrose and of betaine in rice husks.

W. P. S.

Total Amino-nitrogen in the Seedlings of the Alaska Pea. Thos. G. Thompson (*J. Amer. Chem. Soc.*, 1915, **37**, 230—235).—This investigation was undertaken with the object of ascertaining the relation of the total nitrogen to the amino-nitrogen in the growing plant. Estimations of the total and amino-nitrogen in seedlings of the Alaska pea have shown that from the first to the seventh day the percentage of amino-nitrogen increases steadily, and that a marked increase occurs in the first- and fifth-day seedlings. The increase in the case of the first-day seedling is due to the decomposition of the proteins of the seed to afford a supply of food for the new protein material. The increase in the five-day seedling, which at this stage first assumes the form of a regular plant, may be attributed to the rapid transformation of the seed and the consequent need of a larger quantity of food for the formation of the nitrogenous material in the leaves, stems, and roots. As the amino-nitrogen increases at a much greater rate than the total nitrogen, it is evident that there must be a considerable decomposition of the proteins present in the original seed. In the case of the seven-day seedlings, the plumules contain a higher percentage of amino-nitrogen than the radicles, and the latter a much higher percentage than the cotyledons.

The leaves and stems of fourteen-, twenty-one-, and thirty-eight-day plants were analysed, and it was found that, in the fresh leaves, the percentage of total nitrogen remains fairly constant, whilst the amino-nitrogen gradually decreases. If the results are expressed in terms of the dry material, they show a decrease in both total and amino-nitrogen as the plant increases in age.

E. G.

Sensitiveness of Lupins to Calcium. Th. Pfeiffer and E. Blanck (*Bied. Zentr.*, 1915, **44**, 22—25; from *Mitt. landw. Inst. Univ. Breslau*, 1914, **7**, 202).—Whilst ground limestone is less injurious to lupins than precipitated calcium carbonate, its effects vary a good deal, so that it is not possible to show a definite point at which it becomes injurious; in one case the yield was even increased by limestone.

Calcium sulphate is also injurious to lupins, although the amount of calcium taken up by the plants is less with the more soluble sulphate than with limestone. Lupins grown in presence of calcium sulphate contain lower amounts of phosphorus; in presence of limestone and of nitrates, the amounts of phosphorus assimilated are considerably reduced.

Assimilation of iron by lupins is retarded both by limestone and by potassium nitrate, and it is considered probable that the

injurious effects of calcium are partly due to its action on iron assimilation. N. H. J. M.

The Plant Enzymes. III. Changes Produced by Pathological Conditions in the Amylase of Potatoes. G. Doby and J. Bodnár (*Biochem. Zeitsch.*, 1915, **68**, 191—205).—The changes in the concentration of the amylase in potatoes was investigated after varying intervals in the freshly expressed juice, and in juices kept under antiseptic conditions. The results indicated that the ferment exists both in the form of enzyme and zymogen, the former being somewhat sensitive and rapidly destroyed. As long as the bulbs contain excess of zymogen, amylase is set free more rapidly from the zymogen than it is destroyed. For a time, therefore, the amyloclastic activity of the juice increases. Towards spring, however, the amount of zymogen commences to diminish to such an extent that the amount of amylase destroyed becomes greater than that set free, and the amyloclastic activity of the juice diminishes. The amyloclastic activity of the juice kept under antiseptic conditions rapidly diminishes. Healthy plants in general yield juices of greater amyloclastic activity than those infected with the curly leaf disease. S. B. S.

The Gases of Swamp Rice Soils. II. Utilisation for the Aeration of the Roots of the Crop. W. H. Harrison and P. A. Subramania Aiyer (*Mem. Dept. Agric. India, Chem. Ser.*, 1914, **4**, 1—17. Compare *ibid.*, **3**, 65).—It was previously shown that the surface of the soil in contact with the irrigation water is covered by an organised film. This contains bacteria which oxidise methane and hydrogen, and directly assimilate methane and carbon dioxide. Carbon dioxide is produced, and is assimilated by the green algæ, with evolution of oxygen. The soil gases are thus utilised so as to give rise to an increased amount of oxygen, resulting in increased root aeration.

Application of green manure increases the production of soil gases, and hence the activity of the film, followed by an increased supply of soil oxygen. The conclusion is drawn that the oxygen concentration of the soil water is one of the main factors which regulates the growth of the crop; and that green manuring has an important, indirect function in causing increased aeration.

N. H. J. M.

Soil Colloids and the Soil Solution. Frank K. Cameron (*J. Physical Chem.*, 1915, **19**, 1—13).—A discussion of the nature of colloids in relation to the chemistry of soils. Provided that a colloid is defined as a phase sufficiently divided in which surface phenomena are predominant, the chemistry of soils can be considered as a branch of colloid chemistry. The importance of the relation of the gas–liquid surface tension to the solid–liquid surface tension is referred to. That very small changes in the concentration of the soil solution correspond with relatively large changes in the composition of the solid is a necessary consequence of the colloid constitution of the soil. H. M. D.

Changes of Sulphur and Sulphur Compounds in Soils. H. KAPPEN and E. QUENSELL (*Landw. Versuchs-Stat.*, 1915, **86**, 1—34).—When moist soil is treated with hydrogen sulphide, the soil is blackened, owing to the production of iron sulphide, and a portion of the sulphide decomposes with liberation of free sulphur. The iron sulphide then undergoes a process of oxidation, in which all of the sulphur is liberated, so that the whole of the hydrogen sulphide absorbed is converted into free sulphur. The sulphur is then oxidised to sulphuric acid, the change being more rapid in normal than in sterilised soils. It is, however, doubtful whether the slower oxidation of sulphur in sterilised soils is due to the absence of microbes, or to other changes in the soil due to the sterilising process.

Sulphides and sulphites are decomposed more quickly in presence of soil than without soil. In soils the decomposition is so rapid that no injurious effects on germination and growth are to be expected. N. H. J. M.

The Sandy Soil of Sylvan Beach, New York. NICHOLAS KNIGHT (*Chem. News*, 1915, **111**, 49).—The sandy territory at Sylvan Beach, once forming the bottom of the Oneida Lake, is particularly noteworthy on account of the rapidity with which all forms of organic matter in the sand decompose. The hypothesis that the oxidation is brought about by the presence of iron in considerable quantity is not borne out by analyses, of which the following is typical: SiO_2, 91·88; Al_2O_3, 6·28; Fe_2O_3, 1·71; CaO, 0·65; MgO, 0·39; K_2O, 0·04; Na_2O, 0·03; N, H_3PO_4, CO_2, absent. The bacterial content is small, and probably the chief reason for the changes in the sand is the free access of air. G. F. M.

Relation between Total Phosphoric Acid and Citrate-Soluble Phosphoric Acid in Certain Soils of Mid-Peru. A. HUTIN (*Ann. Chim. anal.*, 1915, **20**, 31).—The following summary shows the lowest and highest results obtained on the analysis of a considerable number of samples of Peruvian soils; the citrate-soluble phosphoric acid was estimated by Dyer's method (T., 1894, **65**, 115), and the results are expressed as grams of P_2O_5 per kilo. of fine dry soil:

	Total P_2O_5.	Citrate soluble P_2O_5.	Ratio Soluble/Total.
Soil	2·02 to 2·73	0·78 to 1·45	0·386 to 0·533
Sub-soil ...	1·61 to 2·23	0·74 to 0·98	0·425 to 0·560

One sample (not included in the above) yielded 2·79 grams of total P_2O_5, and 0·10 gram of soluble P_2O_5, whilst the sub-soil gave 2·55 gram of total P_2O_5 and 0·07 gram of soluble P_2O_5; this soil came from a place where animals had been slaughtered and contained bone débris. W. P. S.

Manurial Experiments with Decomposition Products of Calcium Cyanamide. H. KAPPEN (*Landw. Versuchs-Stat.*, 1915, **86**, 115—136).—Experiments, in small garden plots, on the growth of mustard manured with different forms of nitrogen. The

yield with carbamide, prepared from calcium cyanamide (Kappen, Habilitationschr., Jena, 1913), was between those obtained with sodium nitrate and ammonium sulphate, whilst carbamide nitrate gave much lower results; guanidine nitrate gave the smallest yields. The relatively low results obtained with carbamide nitrate were found to be due to the presence of a considerable amount of dicyanodiamidine, produced from dicyanodiamide.

The results of an experiment in which dicyanodiamidine was added to soil showed that very little ammonia was formed in three days, and that no further increase was found in ten days.

N. H. J. M.

Arsenic and Lead in Agriculture. ALESSANDRO CUTOLO (*Bull. chim. farm.*, 1914, **53**, 692—696).—Spraying with solutions or suspensions of arsenic compounds, such as lead arsenate, for the purpose of destroying parasitic organisms, nearly always results in the presence in the foodstuffs obtained, of arsenic (and of lead) in proportions appreciably greater than those naturally present. Extended use of such substances may readily lead to cases of poisoning, and the necessity of prohibiting or regulating their employment is indicated. T. H. P.

Nitrogen and Chlorine in Rain and Snow. WILLIAM K. KNOX (*Chem. News*, 1915, **111**, 61—62).—A continuation of the determinations at Mount Vernon, Iowa, for the period October 4th, 1913, to June 4th, 1914, already commenced by Wiesner for 1912–13 (A., 1914, i, 472). The snow-fall amounted to 11·5 (=0·95 in. water), and the rain-fall to 17·75 inches. In all but a few of the forty-three samples taken, the chlorine was remarkably constant at 10·6 parts per million. Nitrates varied considerably from 0·12 to 1·5 parts per million, averaging about 0·3. Nitrites averaged about 0·001, free and albuminoid ammonia were extremely variable, and in three cases sulphates were found. A table is given showing the amounts falling per acre during the above period, which totals as follows:

	Chlorine.	Nitrates.	Nitrites	Ammonia.	Alb. Ammon	Sulphate.
(lb.).....	36·8488	1·542	0·0129	3·6938	2·7946	0·1292

G. F. M.

Organic Chemistry.

Optical Investigation of Petroleum from Southern Bolivia. II. M. A. RAKUZIN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 58—60. Compare A., 1911, i, 761).—The author has determined the physical properties of petroleum from the Cuarazutti district of S. Bolivia, and of the various fractions obtained on distilling it first at 760 mm. and finally at 7 mm. pressure. In spite of its brownish-black colour, the petroleum has a carbonisation constant approximating to 1 and is, therefore, polarimetrically semi-transparent. This result is in accord with Bonareli's geological data, the occurrence of the petroleum on the surface of the earth indicating that it has undergone a filtration-distillation process and simultaneous aeration. That the latter takes place is supported by the value of D^{15}, namely, 0·8942, and by the results of the distillation. T. H. P.

Optical Investigation of Argentine Petroleum. II. M. A. RAKUZIN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 60—62. Compare A., 1911, i, 761).—Samples of petroleum from Agua Caliente and Ijira were examined. In spite of the relatively high values of D^{15}, namely, 0·9095 and 0·9224 respectively, the carbonisation constants are 1·125 and 1·25, the petroleums being, therefore, semi-transparent. These results, together with the geological data, indicate that, in its passage to the earth's surface, the petroleum is subjected to a complex filtration-distillation process, and is deprived thereby of the greater part of those carbonaceous compounds which retard polarised light. The high value of the density results from aeration of the petroleum.

T. H. P.

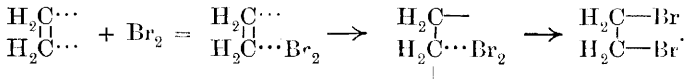
Investigation of Optical Activity of Mineral Oils. C. ENGLER and W. STEINKOPF (*Ber.*, 1914, **47**, 3358—3362).—The authors point out that the detection of optical activity in mineral oils is of considerable importance in its bearing on their possible origin; sporadic activity can be attributed to contact with optically active animal or vegetable matter, but universal activity is a strong argument in favour of an organic origin. Considerable discrepancies exist between the data quoted by various observers for similar oils. In order to obtain definite results, it is necessary that the oil should be separated into as large a number of fractions as possible, and these frequently require to be re-distilled. A superficial fractionation is inadequate, since optically active constituents disseminated through the mass of the oil can escape detection, particularly if both dextro- and lævo-rotatory constituents are present. These precautions are especially important when the maximum activity is to be determined.

It is further shown that mineral oils readily lose their activity, wholly or in part, when exposed to a high temperature; distillation should be effected, therefore, under the smallest possible pressure and from small vessels, superheating being carefully avoided.

Under these circumstances, the authors have found some portions with distinct optical activity in every mineral oil which has been investigated.

It is also pointed out that a similar de-activation may occur in nature, and, therefore, that an oil which is found to be optically inactive may originally have been active. H. W.

Theory of the Formation of Additive Products from Unsaturated Compounds. SIEGMUND REICH (*J. pr. Chem.*, 1914, [ii], **90**, 177—118. Compare A., 1914, i, 42).—It is suggested that the addition of a molecule to an ethylenic linking occurs in three stages. The formation of a molecular additive product by virtue of residual affinities is immediately followed by the opening of the double bond owing to the disturbance in the equilibrium between the forces binding together the carbon atoms. Lastly, the molecular compound changes into an atomic compound by the transference of the reacting atoms to the liberated valencies. The complete process is accordingly represented thus :



This theory of addition allows of an explanation of the phenomena connected with the rearrangement of geometrical isomerides under the influence of certain chemical reagents. If reagents such as the halogens, the halogen hydrides, or nitrous acid, which possess a certain affinity for the ethylene carbon atoms are allowed to react on an unsaturated compound, three results are possible according to the nature of the substances involved. Unsaturated compounds where geometrical isomerism is impossible, and the stable forms of geometrical isomerides react generally as above outlined, whilst the labile geometrical isomerides may react also in this way, if at low temperatures and in the solid state, giving the *cis*-additive product. Under other conditions, two other processes are possible. The labile isomeride after the formation of the molecular compound and the breaking of the double bond may rotate into the stable configuration and then form the atomic compound which is accordingly a derivative of the stable isomeride. But if the reagent employed is such that it has little tendency to unite with the stable form, as, for example, bromine with fumaric or mesaconic acid, then the third possibility will occur, namely, that after the rotation of the molecule the residual valency holding the bromine in molecular combination will be so weakened that instead of atomic addition taking place, the molecule of bromine will be once more split off, leaving the stable geometrical isomeride. To produce this result the reagent employed must obviously possess a suitable relative affinity towards the labile and stable forms, otherwise either an atomic additive product will be formed, or else no reaction will occur at all. The behaviour of chlorine, bromine, and iodine towards *allo*-α-bromo-*m*-nitrocinnamic acid is quoted in illustration of this. Chlorine forms the additive product, bromine converts it in

solution quantitatively into its higher melting isomeride, whilst iodine leaves it entirely unchanged.

Skraup's explanation of the conversion of maleic into fumaric acid by the combined action of hydrogen sulphide and sulphur dioxide on its aqueous solution as being due to the resonance effect set up within the molecule by the chemical reaction in progress in its neighbourhood is held to be quite erroneous. The change, on the contrary, is due to the liberated sulphur, which in a nascent state, before it has polymerised to large molecular aggregates, forms the molecular compound with maleic acid, which breaks down once more after the *trans*-rearrangement, into fumaric acid and sulphur.

The author concludes by extending the theory to the analogous case of addition to an acetylene linking, and also to the reverse process of splitting off halogens or halogen acids with the generation of unsaturated compounds, the same intermediate stages as before being traversed in the reverse direction. G. F. M.

Pyrogenic Acetylene Condensations. Richard Meyer and Hans Fricke (*Ber.*, 1914, **47**, 2765—2774).—The observation that the condensation of acetylene gives rise to some toluene in addition to benzene (A., 1912, i, 525; 1913, i, 1294) has led the authors to a closer examination of the products in the hope of finding other benzene homologues in the condensation product, with the result that systematic fractional distillation of the fraction b. p. 50—150° has yielded styrene together with a liquid, b. p. 138—139·5°, of the formula of xylene. By oxidation of this liquid the presence of *m*- and *p*-xylenes could be proved, because *iso*- and tere-phthalic acids were produced; the presence of *o*-xylene and ethylbenzene was also possible, but could not be proved. It is noteworthy that the xylene of ordinary coal tar consists mainly of the meta- and para-isomerides.

From the higher fractions, α- and β-methylnaphthalenes were separated, and recognised by their picrates, m. p. 141° (compare Lesser, A., 1914, i, 33) and 115° respectively. The presence of 1 : 4-dimethylnaphthalene, b. p. 264—266°, picrate, m. p. 141°, was also detected, and a tetrahydronaphthalene was also isolated, b. p. 193—206°.

The present investigation raises the number of hydrocarbons which are common to the acetylene condensation product and to coal tar, to 23, and the authors believe that the condensation must be a source of some of the coal tar hydrocarbons, although they recognise that it is not the only source (compare Pictet and Bouvier, A., 1913, i, 1315).

An experiment during which air was allowed to enter the apparatus gave certain oxidation products in addition to hydrocarbons, the chief being phenol, acetic acid, and formic acid. D. F. T.

Catalytic Action. H. J. Prins (*J. pr. Chem.*, 1914, [ii], **90**, 276).—A correction to the author's previous communication (A., 1914, i, 648) in which he erroneously stated that Menschutkin had obtained an additive compound of aluminium bromide and ethylene dibromide $C_2H_4Br_2,AlBr_3$. G. F. M.

Dibromodinitromethane as a By-product in the Preparation of Acrylic Esters. ERNST PHILIPPI and EMIL SPENNER (*Monatsh.*, 1915, **36**, 95—96).—The best method for the preparation of esters of acrylic acid is still the old one devised by Tollens and his co-workers, which involves the oxidation of $\alpha\beta$-dibromopropyl alcohol to the corresponding acid. This is a weak point in the scheme, for the agent employed, namely, nitric acid, leads to the formation of a dark oil, which is not "allyl tribromide" as was at first supposed (*Annalen*, 1873, **167**, 239), but dibromodinitromethane. J. C. W.

Preparation of Allyl Alcohol. F. D. CHATTAWAY (T., 1915, **107**, 407—410).—In the usual method for the preparation of allyl alcohol by heating glycerol with oxalic acid, dioxalin is formed intermediately, and at 220—225° it decomposes into carbon dioxide and allyl alcohol. Allyl formate, which always accompanies allyl alcohol in the product, is similarly generated by the decomposition of monoformindioxalin. The best yields of allyl alcohol are obtained under conditions which promote the formation of the normal dioxalins and exclude their hydrolysis to hydrogen oxalates, and the process described in the paper gives yields twice as great as those obtained by Tollen's original method. G. F. M.

Simultaneous Oxidation and Reduction. II. The Decomposition of Trichloromethyl-*R*-carbinols. ARTHUR KÖTZ and C. DIEBEL (*J. pr. Chem.*, 1914, [ii], **90**, 297—314. Compare A., 1913, i, 1309).—The decomposition of carbinols of the type $CCl_3{\cdot}CHR{\cdot}OH$ (where R may be Ph, CN, O:C·OR, NH:C·OR) under the influence of heat, or by the action of tertiary amines or alkali hydroxides, may follow one or more of four courses, depending on the nature of R and of the reagent used.

(1) The splitting off of chloral,

$$CCl_3{\cdot}CHR{\cdot}OH \longrightarrow CCl_3{\cdot}CHO + HR,$$

was observed when cyanotrichloromethylcarbinol was distilled under atmospheric pressure, and also when trichlorolactic acid iminoether was heated.

(2) The splitting off of chloroform,

$$CCl_3{\cdot}CHR{\cdot}OH \longrightarrow CHCl_3 + R{\cdot}CHO,$$

occurred when phenyltrichloromethylcarbinol was heated with triethylamine in a sealed tube at 120°, benzaldehyde constituting the second product of the reaction.

(3) The splitting off of hydrogen chloride,

$$CCl_3{\cdot}CHR{\cdot}OH \longrightarrow HCl + CCl_2{:}CR{\cdot}OH \rightleftharpoons CHCl_2{\cdot}CO{\cdot}R,$$

resulting in the formation of a dichloro-ketone, was observed in the following cases: Phenyltrichloromethylcarbinol on distillation in a stream of carbon dioxide gave dichloroacetophenone, whilst the dry distillation of trichlorolactic acid and sodium trichlorolactate in an atmosphere of carbon dioxide furnished dichloroacetaldehyde, identified by conversion into glyoxime, and glyoxaldisemicarbazone. The action of triethylamine on cyanotrichloromethylcarbinol led to the formation of hydrogen chloride and dichloroacetonitrile, and since an analogous reaction occurred with the acetyl derivative of the above

carbinol leading to the formation of the *acetylcyanohydrin* of *dichloroketen*, $CCl_2{:}C(OAc)\cdot CN$, a colourless liquid, b. p. 78°/6 mm., the conclusion is drawn that the hydrogen atom attached to the carbon, and not the hydroxyl hydrogen atom, is eliminated with chlorine to form the hydrogen chloride. Trichlorolactic acid, and its acetyl derivative, its ethyl ester and the ethyl ether of this ester all lost the elements of hydrogen chloride on suitable treatment with triethylamine (see also A., 1913, i, 1309). In the latter case the hitherto undescribed *ethyl ββ-dichloro-α-ethoxyacrylate* was obtained, b. p. 81—83°/6 mm.

(4) Hydrolysis of the C-chlorine atoms,

$$CCl_3\cdot CHR\cdot OH + 2H_2O \longrightarrow 3HCl + OH\cdot CHR\cdot CO_2H,$$

occurs when hydroxyl ions are present, and therefore was observed only during the action of alkali hydroxides on the carbinols. Thus phenyltrichloromethylcarbinol gave mandelic acid, and trichlorolactic acid iminoether, and its ethyl ester, and tartronic acid. On the other hand, chloral cyanohydrin and trichlorolactic acid when treated with alkali hydroxide underwent decomposition (3) and gave dichlorolactic acid and dichloropyruvic acid or dichloroacetaldehyde respectively.

In addition to the substances already mentioned, the following lactic acid derivatives were also prepared. *βββ-Trichlorolactic acid iminoether hydrochloride* was prepared from chloral cyanohydrin in the usual way. It decomposed at 122—123° without melting, and was converted into ethyl trichlorolactate on warming with water. The free iminoether was obtained by treating the hydrochloride with solid potassium hydroxide and extracting with dry ether in a Soxhlet apparatus. It decomposed on heating without melting, and the hope that on distillation or by treatment with triethylamine it would lose hydrogen chloride and yield the iminoether of a dichloro-α-ketonic acid was not realised. On distillation in a stream of hydrogen chloride, it was decomposed into ethyl chloride and *βββ-trichlorolactamide*, m. p. 95—96°. G. F. M.

Condensation of Acetone and Benzaldehyde with Glycerol. Preparation of Glycerol α-Methyl Ether. J. C. Irvine, J. L. Macdonald, and C. W. Soutar (T., 1915, **107**, 337—351).—Acetone glycerol obtained first by Fischer by condensing glycerol and acetone in the presence of hydrochloric acid (A., 1895, i, 441) may have either of the two structures

(I) $OH\cdot CH\langle\begin{matrix}CH_2\cdot O\\CH_2\cdot O\end{matrix}\rangle CMe_2$ or (II) $\begin{matrix}&CH_2\cdot O\\OH\cdot CH_2\cdot CH&\!\!-\!\!-O\end{matrix}\rangle CMe_2$

This point has now been decided in favour of II by converting the compound into its methyl ether, and submitting this to hydrolysis, whereby glycerol-α-methyl ether was obtained.

Glycerol isopropylidene ether (acetone glycerol) was obtained as a colourless liquid, b. p. 86·5°/13 mm., n_D 1·4383, D_4^{18} 1·0727. By shaking with silver oxide and methyl iodide only a *monomethyl ether* could be obtained, b. p. 57°/13 mm., n_D 1·4177, D_4^{15} 0·9900. This disposes of structural schemes based on the reaction of acetone in the enolic form. This ether on hydrolysis by boiling with 0·5% hydrochloric acid in aqueous alcohol gave *glycerol-α-methyl ether*, a colourless neutral liquid, soluble in water and organic solvents: b. p. 110°/

13 mm.; n_D 1·4463, D_4^{17} 1·1197. Attempts to elucidate the constitution of this ether by proving it to be capable of resolution were unsuccessful, as the phthalic acid esters were incapable of individual isolation, and the *l*-menthone condensation product, l-*menthylidene glycerol methyl ester* was a liquid, b. p. 135—136°/11 mm., which could not be obtained crystalline. Finally, its structure was established by synthesis from allyl iodide by the following reactions:
$CH_2{:}CH{\cdot}CH_2I \longrightarrow CH_2{:}CH{\cdot}CH_2{\cdot}OMe \longrightarrow CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}OMe \longrightarrow OAc{\cdot}CH_2{\cdot}CH(OAc){\cdot}CH_2{\cdot}OMe \longrightarrow OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OMe$.
Methyl allyl ether, has b. p. 42·5—43°/757 mm., and n_D 1·3778—1·3803. *βγ-Dibromo-α-methoxypropane*, obtained by brominating the latter, had b. p. 81°/16 mm., D_4^{20} 1·8329, n_D 1·5143. The glycerol methyl ether obtained from this substance had physical constants identical with those of the ether obtained from the acetone glycerol ether, and the position of the methoxy-group was thus established.

Benzylidene glycerol ether, prepared by the condensation of benzaldehyde and glycerol, formed pointed prisms, m. p. 65°, b. p. 140°/0·07 mm., and gave a *monomethyl ether*, b. p. 121°/1·6 mm. This was extremely readily hydrolysed and gave likewise glycerol α-methyl ether, whence it follows that the constitution of the benzylidene glycerol is analogous to that of glycerol *iso*propylidene ether.

G. F. M.

Preparation of Optically Active Fats. II. Synthesis of Optically Active Monobromohydrin, Epihydrin Alcohol, Aminopropanediol, and Propionin. Emil Abderhalden and Egon Eichwald (*Ber.*, 1914, **47**, 2880—2888. Compare *ibid.*, 1856).—A description of synthetic methods of preparing a number of optically active substances. Bromination of allylamine, obtained from allyl thiocarbimide yielded dibromoaminopropane, the dextrorotatory modification being isolated from the mixed tartrates. The *d*-tartrate has $[\alpha]_D$ +34·73°, and the corresponding *d*-dibromohydrin has D 0·839 and $[\alpha]_D$ +7·27°. This dibromohydrin is obtained from *d*-dibromoaminopropane by diazotisation. Warming with concentrated aqueous potassium hydroxide converts the active dibromohydrins into the corresponding active epibromohydrins, but the transformation is attended by a considerable degree of racemisation. The purest *d*-product obtained had D 1·615 and $[\alpha]_D$ +14·48°. The purest *l*-epibromohydrin had $[\alpha]_D$ −4·99°. Three esters of *d*-dibromohydrin have been prepared: *dibromohydrin-α-propionin*, D 0·8374, $[\alpha]_D$ +7·51°; *dibromohydrin-α-caprin*, D 0·8415, $[\alpha]_D$ +7·17°; *dibromohydrin-α-stearin*, D 0·8149, $[\alpha]_D$ +4·62°.

The active epibromohydrins can be converted into the corresponding monobromohydrins by the action of formic acid, and saponification of the formylmonobromohydrin to $CH_2Br{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$. d-*α-Monobromohydrin* has D 0·8318 and $[\alpha]_D$ +3·24°. l-*α-Monobromohydrin* has D 1·0214 and $[\alpha]_D$ −0·49°. d-*Dicaproyl-α-bromohydrin* has D 0·8014, and $[\alpha]_D$ −1·85°.

Elimination of hydrogen bromide from *d*-monobromohydrin by Nef's method (A., 1905, i, 3) yields a small proportion of d-*epihydrin-alcohol*, D 0·801, $[\alpha]_D$ −1·81°, the sign of rotation being inverted. l-*Epihydrin*

alcohol is formed similarly from *l*-monobromohydrin, the racemisation being less than with the *d*-compound. The *l*-derivative has D 0·8562, and $[\alpha]_D$ +1·20°.

d- and *l*-Aminopropanediol, $NH_2 \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH$, are formed from the corresponding epihydrin-alcohol by the action of aqueous ammonia according to the method of L. and Ed. Knorr (A., 1899, i, 411). The amount of the *d*-compound obtained was too small to determine its constants, but *l*-aminopropanediol has D 1·0231 and $[\alpha]_D$ −1·34°.

Prolonged action of propionic acid on *d*-epihydrin-alcohol yields a dextrorotatory ester, *monopropionin* or *dipropionin*, not yet investigated. It is the first synthetic, optically active fat. A. J. W.

Constitution of the Glycerophosphoric Acid of Lecithin. O. Bailly (*Compt. rend.*, 1915, **160**, 395—398. Compare Willstätter and Lüdecke, A., 1904, i, 1067; Fourneau and Piettre, A., 1912, ii, 1109).—The author has prepared calcium glycerophosphate from egg lecithin, and has found by the method already described (this vol., i, 73) that it is a mixture of calcium salts of the α- and β-acids. Egg lecithin is therefore a mixture of two isomerides having the constitutions $OH \cdot C_2H_4 \cdot NMe_3 \cdot O \cdot PO(OH) \cdot O \cdot CH_2 \cdot CH(OR) \cdot CH_2 \cdot OR$ and $OH \cdot C_2H_4 \cdot NMe_3 \cdot O \cdot PO(OH) \cdot O \cdot CH(CH_2 \cdot OR)_2$, where R is a fatty acid residue, of which the second form predominates. W. G.

Chemical Kinetics of Formic Acid Formation. G. Bredig (*Zeitsch. Elektrochem.*, 1914, **20**, 489—494).—A general survey of the formation of formates by the action of carbon monoxide on bases. When carbon monoxide acts on strong bases such as sodium hydroxide, potassium hydroxide, tetramethylammonium hydroxide, and tetraethylammonium hydroxide at 50—80° and pressures up to 40 atms., the reaction constant shows that neither the hydroxyl ions nor the undissociated alkali molecules alone are the active agents in the reaction. With weak bases such as piperidine, diethylamine, and *iso*butylamine, although the hydroxyl ions are chiefly instrumental in the reaction, yet they are not alone responsible for the reaction. But if the reaction constant is calculated on the hypothesis that both hydroxyl ions and undissociated bases are concerned in the reaction, then satisfactory figures are obtained. The constant for the action of the hydroxyl ions, k_{OH}, is independent of the nature of the base, the following figures being obtained for k_{OH} at 80°: NaOH, 0·0684; KOH, 0·0690; $NMe_4 \cdot OH$, 0·0730; $Ba(OH)_2$, 0·0720; piperidine, 0·0810; diethylamine, 0·0730; and *iso*butylamine, 0·0710. If k_m represents the reaction constant of the undissociated molecules then the ratio $k_m : k_{OH}$ for the bases investigated is given by the figures KOH, 2·2; $NEt_4 \cdot OH$, 1·9; NaOH, 1·1; $Ba(OH)_2$, 0·68; piperidine, 0·0039; diethylamine, 0·0045, and *iso*butylamine, 0·0026. The result here is the same as that found by Snethlage (A., 1913, ii, 1044), namely, that with strong bases the action of the hydroxyl ions and undissociated molecules is of about the same dimensions, whereas with weak bases the action of the undissociated molecules is very much less. It is shown that there are some points in the process still

unexplained which in all probability depend on the presence of more than one kind of undissociated molecule. J. F. S.

The Molecular Complexity of Acetic Acid. G. M. BENNETT (*T.*, 1915, **107**, 351—360).—A redetermination of the surface tension of acetic acid between 15° and 150° has been made, the method adopted being that depending on the measurement of capillary rise in the absence of air, using a modification of the apparatus described by Hewitt and Winmill (T., 1907, **91**, 441). The results lay between 27·90 at 20° and 15·17 at 150°, and when plotted against temperatures the curve was found to be a straight line. The values are slightly higher than those obtained by Ramsay and Shields and by Worley, and it is suggested that this is due to the greater purity of the acid employed in this case. The value of k calculated from the equation $k=d[\gamma(Mv)^{\frac{2}{3}}]/dt$ is sensibly constant over the whole range of temperature, being 1·275 at 25°, 1·265 at 85°, and 1·250 at 145°, whilst the function $(\gamma - t[d\gamma/dt])(Mv)^{\frac{2}{3}}$, which the author regards as a better criterion of normality (compare A., 1913, ii, 927), varies only from 871 to 883 ergs. Hence acetic acid is a normal liquid between 15° and 150°, and the double molecule, $(C_2H_4O_2)_2$, behaves as a single stable molecule throughout. The alternative possibility to regarding acetic acid as a pure bimolecular liquid, the degree of association of which is unchanged within the above temperature range, is that of a liquid in a state of equilibrium such as $(C_2H_4O_2)_2 \rightleftharpoons 2C_2H_4O_2$, which is unchanged by alterations in temperature. This possibility is, however, rejected, since it is not in accord with the facts, namely, that at 180° acetic acid vapour is entirely unimolecular. The union of the two molecules in liquid acetic acid must be of a relatively stable character, although it vanishes when the acid is dissolved in water or other hydroxylic solvents. The binacetates, $MC_2H_3O_2,C_2H_4O_2$, are derivatives of this complex, and likewise show considerable stability. The homologues of acetic acid are probably in a similar condition in the liquid state to that of acetic acid itself. G. F. M.

The Biochemistry of the Action of Rays. III. The Formation of Carbonates of Alkali from Neutral Salts in the Light. C. NEUBERG and W. H. PETERSON (*Biochem. Zeitsch.*, 1914, **67**, 63—70).—When solutions of potassium salts of organic acids (malate, succinate, citrate or lactate) or potassium sodium tartrate are exposed to light and air in the presence of catalysts (ferrous sulphate, ferric sulphate, uranyl sulphate, manganous sulphate, sodium anthraquinone-2 : 7-disulphonate, and 9 : 10-dichloroanthracene-2 : 7-disulphonate) an increase in the alkalinity of the solution is observed. As an example of the method of formation of the alkali, the following equation may be given: $CH_3{\cdot}CH(OH){\cdot}CO_2Na + O = CH_3{\cdot}CHO + NaHCO_3$. The solutions employed were sterilised before exposure. S. B. S.

Chemical Actions of Penetrating Radium Rays. IX. Influence of the Penetrating Rays on Aqueous Solutions of Fumaric and Maleic Acids. A. KAILAN (*Monatsh.*, 1915, **36**, 13—27).—Solutions of maleic and fumaric acids were left with radium preparations

(80·5 mg. and 110·4 mg. metal) and the conductivity and titration value determined at various intervals. The conductivity of fumaric acid solutions increased, whilst that of maleic acid decreased, showing that transformation of one acid into the other takes place just as in ultra-violet light. The fall in the titration figure was, however, greater in the case of fumaric acid than with maleic acid, which is the opposite of the effect produced by ultra-violet light. The solutions also developed the capacity to reduce silver solutions. The influence of the formation of an aldehyde, aldehydic acid, or of acrylic acid on the calculations of the speed of transformation is discussed at some length, and it is shown that, even in the extreme case, the mutual transformation is about equal, that is, the equilibrium favours fumaric acid much more than is the case with ultra-violet light. The transformation of maleic into fumaric acid is about eight hundred times, and the reverse process about seven thousand times, as slow as in ultra-violet light. J. C. W.

Influence of Light on the Polymerisation of Ethyl Itaconate. Hans Stobbe and Alfred Lippold (*J. pr. Chem.*, 1914, [ii], **90**, 336—344).—By the spontaneous polymerisation of ethyl itaconate an amorphous polymeride of unknown, but certainly high molecular weight is formed. The course of the polymerisation was followed by measurements of the refractive index. The pure ester, b. p. 134°/40 mm., $n_C^{20} = 1{\cdot}43609$, had acquired, after periodical illumination by sunlight in a quartz vessel for sixty-five days, a refractive index of 1·44928, whilst a similar preparation in the dark was unchanged. In addition to this accelerating effect of light, the presence of traces of hydrogen chloride also increased the rate of polymerisation, and in both cases the velocity increased as the reaction proceeded. It is therefore an autocatalytic process, but of the nature of the autocatalyst nothing definite could be ascertained. The poly-itaconic acid ethyl ester is an odourless and colourless, glassy substance; it is soluble in the monomeric ester, forming a viscous liquid similar to that obtained in the early stages of the polymerisation. From these viscous solutions the polymeride may be precipitated by alcohol, and lower intermediate products of polymerisation were never observed. The glassy poly-ester has an unsaturated character, and furnishes by hydrolysis with acids or alkalis a water-soluble, unsaturated acid. It cannot be depolymerised by distillation, as even in vacuum it suffers a far reaching decomposition, yielding volatile products of unknown composition. G. F. M.

Tetra-acetylmucyl Chloride and its Application to the Synthesis of Inositol. Otto Diels and Fritz Löflund (*Ber.*, 1914, **47**, 2826—2827).—A reply to the claim of Müller (*ibid.*, 2655) for priority. D. F. T.

Cystine Nitrate and Cystine Hydrochloride. Carl Th. Mörner (*Zeitsch. physiol. Chem.*, 1914, **93**, 203—208).—Cystine nitrate (from cystine and nitric acid at room temperature) has the composition

$C_6H_{12}O_4N_2S_2,2HNO_3$, and the hydrochloride the formula $C_6H_{12}O_4N_2S_2,2HCl$.

R. V. S.

Lithofellic acid. HANS FISCHER (*Ber.*, 1914, **47**, 2728—2729).—The concretions from which the so-called lithofellic acid was obtained (Jünger and Klages, A., 1896, i, 194), which were believed to be gall-stones derived from cattle, are in reality of intestinal origin. The formula of lithofellic acid is $C_{24}H_{42}O_5$ (or $C_{24}H_{44}O_5$) and not $C_{20}H_{36}O_4$ as previously suggested; the acid probably owes its formation to reduction of cholic acid. It is monobasic, has m. p. 205—206°, and $\alpha_D^{20} + 13{\cdot}1°$. D. F. T.

The Formation of Aldehydes by Potassium Permanganate. E. SALKOWSKI (*Biochem. Zeitsch.*, 1914, **67**, 349—356).—The author was unaware of Rosenthaler's previous work on this subject (A., 1914, i, 248). His results confirm those of Rosenthaler. S. B. S.

Simple Isomeric Changes of the Glycols and their Nitrogenous Derivatives. I. The Formation of Acetaldehyde from Ethylene Glycol, Ethylenediamine, Colamine, Serine and *iso*Serine. C. NEUBERG and B. REWALD (*Biochem. Zeitsch.*, 1914, **67**, 127—136).—By the action of nitrous acid on aminoethylalcohol (colamine) ethylenediamine, serine, and *iso*serine, relatively large amounts of acetaldehyde are produced. Ethylene glycol can also give rise to this aldehyde when it is treated with hydrogen peroxide in the presence of an iron salt, the method being similar to that employed when acetaldehyde is produced from tartaric acid. The reaction between the amino-acids and nitrous acid gives rise to acetaldehyde at relatively low temperatures, 40°. The mechanism of the reaction is discussed by the authors, who call attention to the fact that a simple method has been discovered of converting the group $CH_2(OH)\cdot CH(OH)-$ into the group $CH_3\cdot CH<$. This change, although up to the present rarely accomplished by simple laboratory methods, often takes place in biochemical reactions, such as the conversion of sucrose into ethyl alcohol or butyric acid by various fermentative processes. S. B. S.

The Biochemistry of the Action of Rays. II. A Characteristic Formation of Acetaldehyde from Different Aliphatic Acids by Photocatalytic Processes. C. NEUBERG (*Biochem. Zeitsch.*, 1914, **67**, 59—62).—Acetaldehyde was obtained from the following substances when their solutions were exposed to bright sunlight and air in the presence of small amounts of ferrous sulphate: Propionic, *dl*-glyceric, succinic, maleic, fumaric, *d*-tartaric, α-crotonic acids, *dl*-serine and *dl-iso*serine. A catalyst such as the iron salt is absolutely necessary for the reaction. S. B. S.

The Degradation of Succinic and α-Crotonic Acids to Acetaldehyde. C. NEUBERG [with C. TOMINAGA] (*Biochem. Zeitsch.*, 1914, **67**, 71—76).—From both succinic and α-crotonic acids,

acetaldehyde can be obtained by oxidation with hydrogen peroxide in the presence of ferrous sulphate. In the case of the former acid a yield of up to 7·7% of the aldehyde was obtained (about 20% of the theoretical), and in that of the latter acid up to 9·5% (18·5% of the theoretical). Attention is called to the similarity of this oxidation process and the photocatalytic oxidation by air. The mechanism of the oxidation is discussed. S. B. S.

The Conversion of Fumaric, Maleic, Glyceric, and Tartaric Acids into Acetaldehyde. Carl Neuberg and Olga Rubin (*Biochem. Zeitsch.*, 1914, **67**, 77—81).—This conversion was effected by means of hydrogen peroxide and ferrous sulphate by a method similar to that employed for the oxidation of succinic and α-crotonic acids (compare Neuberg, preceding abstract). S. B. S.

Formation of Anhydrides of the Mono-esters of ωω-Glycols from Aldehydes. Ernst Späth (*Monatsh.*, 1915, **36**, 29—43).—When phenylacetaldehyde is treated with acetic anhydride there is formed, under certain conditions, besides the normal diacetate, the anhydride, $O[CH(OAc)\cdot CH_2Ph]_2$ (Wegscheider and Späth, A., 1910, i, 155; Wohl and Maag, A., 1911, i, 13). Other aldehydes have now been examined, but it is found that only a few are capable of forming such anhydrides. It seems certain that the polymerisation of the aldehyde plays an important part in the reaction, for only those aldehydes which readily polymerise behave in this way. The critical compound is supposed to be the dimeride of the aldehyde, which is regarded as a labile substance with a weak oxygen bridge, thus, RCH·O·CHR.



If the addition of the acid anhydride takes place rapidly, that is, before the dimeride can polymerise further, the anhydride is formed. Thus, whilst acetic anhydride converts phenylacetaldehyde into the above anhydride, chloroacetic and benzoic anhydrides react too slowly to effect this. Conversely, polymerised aldehydes may also react in this way during their depolymerisation.

Trioxymethylene was heated with acetic anhydride and a few drops of concentrated sulphuric acid for seven hours at 200°, when the product was shaken with sodium acetate solution and the residual oil extracted with ether and distilled. The fractions obtained consisted of methylene diacetate, b. p. 62—64°/11 mm., the compound, $O(CH_2\cdot OAc)_2$, b. p. 99—103°/11 mm., and the compound, $CH_2(O\cdot CH_2Ac)_2$, b. p. 127—130°/11 mm. (Grassi-Cristaldi and Maselli, A., 1899, i, 409).

Paraldehyde was left for five days with acetic anhydride and sulphuric acid, and then the product was worked up as above. Acetaldehyde, ethylidene diacetate, b. p. 65—67°/10 mm. (Wohl and Maag, *loc. cit.*, gave b. p. 58°/12 mm.), and aldol monoacetate, b. p. 81—83°/11 mm. (Wegscheider and Späth, A., 1911, i, 112), were the substances obtained. Similarly, chloroacetaldehyde yielded *chloroethylidene diacetate*, $CH_2Cl\cdot CH(OAc)_2$, b. p. 95—97°/10 mm., and, probably, dichlorocrotonaldehyde diacetate, $C_8H_{10}O_4Cl_2$, b. p. 110—113°/13 mm. Chloral,

*iso*butaldehyde and cinnamaldehyde also yielded the diacetates when left with cold acetic anhydride.

When phenylacetaldehyde was left with the required quantity of acetic anhydride in the cold, the anhydride, $O[CH(OAc)\cdot CH_2Ph]_2$, was deposited in shining leaflets, m. p. 126—127°. This is converted into phenylethylidene diacetate by excess of acetic anhydride and into the hydrazone or oxime of phenylacetaldehyde by warming with phenylhydrazine or hydroxylamine. By employing a large excess of acetic anhydride (25 c.c. to 5 g. of phenylacetaldehyde) the diacetate forms the main product, the yield being about 70%. Wohl and Maag (*loc. cit.*), who recommended a slight excess of acetic anhydride, obtained a 15% yield. J. C. W.

d- and *l*-Glyceraldehyde. A. Wohl and Fr. Momber (*Ber.*, 1914, **47**, 3346—3358).—r-*β-Aminolactaldehyde dimethylacetal* has been converted by *l*-menthylcarbimide into a mixture of the corresponding active carbamides which can be separated into its components by means of ether. Hydrolysis of the active carbamides by methyl-alcoholic potassium hydroxide yields d- and l-*aminolactaldehyde dimethylacetals*, which are converted by nitrous acid into d- and l-*glyceraldehyde dimethylacetals*. The corresponding aldehydes have been obtained in a non-crystalline state from the latter.

β-Chloropropaldehyde dimethylacetal, $CH_2Cl\cdot CH_2\cdot CH(OMe)_2$, b. p. 86°/100 mm., D^{18} 1·2051 (compare Emmerich, *Diss.*, Berlin, 1902), is obtained by the action of a solution of hydrogen chloride in methyl alcohol on acraldehyde, and is converted by powdered potassium hydroxide into acraldehyde dimethylacetal, b. p. 86°/760 mm., D^{18} 0·862 (compare Moers, *Diss.*, Berlin, 1907). The latter yields *α*-chloro-*β*-hydroxypropionaldehyde dimethylacetal when treated with hypochlorous acid (Wohl and Schweitzer, A., 1907, i, 194), which, when distilled with solid potassium hydroxide, gives *epihydrinaldehyde dimethylacetal*, $CH_2\text{–}CH\cdot CH(OMe)_2$ (O), b. p. 146—147°/760 mm. Attempts to obtain the latter by direct oxidation of the acraldehyde-acetal by benzoylhydroperoxide, hydrogen peroxide, or sodium peroxide were unsuccessful.

The action of a methyl-alcoholic solution of ammonia on the epihydrin acetal yields a mixture of *β*-aminolactaldehyde dimethylacetal, m. p. 58°, and of an imide, $HN[CH_2\cdot CH(OH)\cdot CH(OMe)_2]_2$, b. p. 195—198°/12 mm., m. p. 47°. Attempts to resolve the racemic amine into its optical antipodes by means of tartaric acid, diacetyltartaric anhydride, malic acid, quinic acid, saccharic acid or bromocamphorsulphonic acid were unsuccessful.

l-*Menthyl*-d-*β-hydroxypropionacetalylcarbamide*, $C_{10}H_{19}\cdot NH\cdot CO\cdot NH\cdot CH_2\cdot CH(OH)\cdot CH(OMe)_2$, m. p. 149°, $[\alpha]_D^{19}$ −36·9° in alcoholic solution, and l-*menthyl*-l-*β-hydroxypropionacetalylcarbamide*, m. p. 69°, $[\alpha]_D^{19}$ −72·8° in alcohol, are obtained by the action of *l*-menthylcarbimide on *β*-aminolactaldehyde dimethylacetal in ethereal solution; under suitable conditions of concentration, the *d*-isomeride separates in an approximately pure state. Fission of

the carbamides is effected by potassium hydroxide in aqueous methyl-alcoholic solution at 160°; racemisation does not appear to occur. d-*Aminolactaldehyde dimethylacetal* is exceedingly hygroscopic. It has m. p. 43°, $[\alpha]_D^{18}$ +21·5° in water. The corresponding l-*amine* has m. p. 42°, $[\alpha]_D^{25}$ −20·5°, and appears to contain small quantities of the *d*-isomeride. Attempts to resolve the carbamide by urease in the form of the crushed seeds of the soja bean or of *Robinia pseudocacia* at the ordinary temperature were unsuccessful.

d-*Glyceraldehyde dimethylacetal*, b. p. 124—127°/14 mm., $[\alpha]_D^{22}$ +21·8° in aqueous solution, and l-*glyceraldehyde dimethylacetal*, b. p. 126—129°/17—20 mm., $[\alpha]_D^{25}$ −20·9°, when dissolved in water, are prepared by the addition of 5*N*-acetic acid to an aqueous solution of the corresponding amine and sodium nitrite at 0°. The yields are not particularly good. As by-products, the *ketone*, $CH_3 \cdot CO \cdot CH(OMe)_2$, b. p. 143—147°/760 mm. (identified also by conversion into the osazone of methylglyoxal), and an optically active *substance*, $C_{10}H_{22}O_6N_2$, pale viscous oil, b. p. 170—174°/13 mm., 118—120°/0·6 mm., were isolated.

The active glyceraldehydes are prepared by treatment of the corresponding acetals with *N*/10-sulphuric acid at the ordinary temperature. They form pale syrups which could not be caused to crystallise, and which possess marked tendencies towards polymerisation. A freshly-prepared specimen of the *d*-aldehyde had $[\alpha]_D$ about +24°. H. W.

Preparation of Acetone Diethylacetal. L. Claisen (*Ber.*, 1914, **47**, 3171—3172).—Tschitschibabin and Jelgasin (A., 1914 i, 1066) recently stated that they found a difficulty in condensing acetone with ethyl formate and alcohol by Claisen's method (A., 1907, i, 940) and they employed sulphuric acid as the condensing agent. The author now gives fuller details of his process and shows that the original catalyst, ammonium chloride, is as suitable as a mineral acid.

J. C. W.

Acids and Colloids of Humus. Gustav Fischer (*Bied. Zentr.*, 1914, **43**, 660—665; from *Kühn-Arch.*, 1914, **4**, 1—136).—The colloids were obtained from peat and from cultivated black soil by extracting with cold or hot water and filtering through hardened paper filters. After concentrating the solution in a vacuum at 30° it was further purified by dialysis through parchment. As regards the mineral constituents, alumina, manganese and silica were not found. The substances found to be present are iron, calcium, potassium and sodium and small amounts of magnesium and phosphorus. The total ash amounted to 8·6—23·3% of the dry matter of the colloidal substance.

The humus colloids examined were found to be without protective action on gold hydrosols, which is the most important property of the reversible, organic colloids. This may, perhaps, be considered to confirm, indirectly, the non-emulsoid form of humus colloids.

N. H. J. M.

Quadrivalent Lead. A. Gutbier and M. Wissmüller (*J. pr. Chem.*, 1914, [ii], **90**, 491—508).—The authors have made a systematic

study of the plumbichlorides, prepared by mixing solutions of the corresponding acid, H_2PbCl_6 (compare Elbs and Nübling, A., 1903, ii, 727), with solutions of the chlorides of the metals or bases.

These compounds are anhydrous and correspond with the general formula X_2PbCl_6 or $(R{\cdot}NH_3)_2PbCl_6$. They crystallise immediately from the mixed solutions, but the crystals are usually extremely small or intermixed, and as no embedding material could be found devoid of action on the compounds, crystallographic measurement was difficult. In those cases where the crystalline system could be ascertained, regular and rhombic forms predominate. The compounds of the alkali metals and of derivatives of the pyridine and quinoline series are especially stable, whilst the aliphatic ammonium compounds tend to decompose in the air, the crystals gradually becoming white and chlorine being evolved. With the exception of the potassium salt, which undergoes such hydrolysis only when freshly prepared, all the compounds prepared by the authors behave towards water in the manner already described for ammonium plumbichloride (compare Gutbier and Sauer, A., 1913, ii, 505). Hydrogen peroxide exerts an immediate reducing action, plumbous chloride being separated and gas evolved. Concentrated ammonia solution yields a light brown, and a dilute solution, an almost black precipitate containing lead dioxide. Towards sulphuric acid and alcohol, these compounds behave in the manner described by Friedrich (A., 1893, ii, 415; 1894, ii, 16) and by Classen and Zahorski (A., 1893, ii, 464). Contrary to the statements of Wells (A., 1893, ii, 524) and of Elbs and Nübling (*loc. cit.*), the potassium salt is bright orange-red and forms twinned crystals apparently of the monoclinic system.

The following plumbichlorides have been prepared and analysed. Ammonium, pale yellow in the cold, intense orange-red at 100°; potassium; rubidium; cæsium; *methylammonium*, $(NH_3Me)_2PbCl_6$, dirty yellow, irregular crystals; *dimethylammonium*, $(NH_2Me_2)PbCl_6$, slender, pale yellow needles of the tetragonal or rhombic system; *trimethylammonium*, pale yellow octahedra of the regular system; *tetramethylammonium*, pale yellow crystalline precipitate; *ethylammonium*, shining, lemon-yellow, irregular leaflets; *diethylammonium*, conglomerate of lemon-yellow leaflets and needles; *triethylammonium*, intensely yellow, well-formed, monoclinic plates; *tetra-ethylammonium*, powdery, yellow precipitate; n-*propylammonium*, small, pale yellow, tetragonal or rhombic prisms; iso*propylammonium*, unstable, pale yellow crystals; *dipropylammonium*, pale yellow, apparently monoclinic crystals; *tripropylammonium*, orange-yellow, rhombic prisms; n-*butylammonium*, lustrous yellow, crystalline powder; iso*butylammonium*, pale yellow powder; *di*-iso*butylammonium*, yellow, unstable powder; *tri*-iso*butylammonium*, small, bright yellow, felted needles; *allylammonium*, long, yellow, highly unstable needles; iso*amylammonium*, slender, yellow, felted needles, rapidly decomposing; *di*-iso*amylammonium*, yellow crystals of the regular system; *tri*-iso*amylammonium*, indefinite, wine-yellow crystals; *ethylenediammonium*,

$$[C_2H_4(NH_3)_2]PbCl_6,$$

yellow, crystalline powder; *propylenediammonium*, indefinite, yellow, crystalline powder; pyridinium (compare Classen and Zahorski, *loc.*

cit.), lemon-yellow, acicular prisms, apparently triclinic; *α-picolinium*, $(C_5NH_5Me)_2PbCl_6$, pale yellow needles of the rhombic system; *β-picolinium*, pale yellow, rhombic prisms; *lutidinium*,

$$(C_5NH_4Me_2)_2PbCl_6,$$

pale yellow, rhombic prisms; *collidinium*, $(C_5NH_3Me_3)_2PbCl_6$, intensely yellow, rhombic prisms, isomorphous with the lutidinium compound; quinolinium (compare Classen and Zahorski, *loc. cit.*; Elbs and Nübling, *loc. cit.*), long, lemon-yellow needles; iso*quinolinium*, long, yellow needles. T. H. P.

Betaine. Hugo Stoltzenberg (*Zeitsch. physiol. Chem.*, 1914, **92**, 445—494).—The author has prepared a large number of salts and compounds of betaine, and has determined the solubility of many of them at various temperatures, and also the axial relations of their crystals.

Betaine is obtained from betaine hydrochloride (A., 1912, i, 680) by first transforming it into the sulphate and then treating with the calculated quantity of barium hydroxide. The betaine is recrystallised from alcohol and dried at 100° in a vacuum. Its heat of solution is +1385 cal. It readily absorbs one mol. of water on exposure to the air, and is then no longer hygroscopic. The water of crystallisation is readily replaced by hydrogen peroxide by simply mixing betaine with twice its weight of 30% hydrogen peroxide and evaporating at 50—60° in vacuum. The crystals rapidly effloresce in the air. A new *basic betaine hydrochloride-hydrogen peroxide* compound,

$$(C_5H_{11}O_2N)_2,HCl,H_2O_2,$$

is more stable, and retains its crystalline form and lustre in the air.

The following new salts of betaine have been prepared in most cases by evaporation of a mixture of aqueous solutions of their components: *hydrofluoride*, $C_5H_{11}O_2N,HF$; *acid hydrofluoride*, $C_5H_{11}O_2N,2HF$; *basic hydrochloride*, $(C_5H_{11}O_2N)_2,HCl,H_2O$, flat, monoclinic prisms, m. p. 250°; *hydrobromide*, prisms, m. p. 233° (decomp.); *basic hydrobromide*, $(C_5H_{11}O_2N)_2,HBr$, minute, anhydrous prisms, m. p. 262°; *basic hydriodide*, $(C_5H_{11}O_2N)_2,HI$, snow-white, glittering plates, m. p. 242°. Besides the simple aurichloride, a *basic aurichloride*,

$$5C_5H_{11}O_2N,4HAuCl_4,H_2O,$$

is obtained by evaporating in the presence of excess of betaine; yellow, crystalline powder, m. p. 169° (decomp.), and also a *betaine-gold chloride* compound, $C_5H_{11}O_2N,AuCl_3$, yellow needles, m. p. 172·5°, which falls as a yellow precipitate when solutions of gold chloride and betaine are mixed together. *Basic auribromide*,

$$(C_5H_{11}O_2N)_5,4HAuBr_4,$$

dark red, amorphous powder, m. p. 185°; *auribromide*,

$$C_5H_{11}O_2N,HAuBr_4,$$

dark brown plates, m. p. 260° (decomp.), obtained from the basic auribromide by warming with hydrobromic acid.

The following platinum derivatives have been obtained: platinichloride in two crystalline forms, $C_5H_{11}O_2N,H_2PtCl_6,4H_2O$, orange-yellow crystals, m. p. 254·5°, and $C_5H_{11}O_2N,H_2PtCl_6,3H_2O$, large, yellow, monoclinic prisms, m. p. 255—260°; *basic platinichloride*, $(C_5H_{11}O_2N)_5,4H_2PtCl_6$, orange crystals, m. p. 246° (decomp.), and a

betaine platinum chloride compound, $C_5H_{11}O_2N,PtCl_4,3H_2O$, minute, yellow crystals, m. p. 209° (decomp.). Other compounds prepared were the *phosphate*, $C_5H_{11}O_2N,H_3PO_4$, monoclinic prisms, m. p. 199°; *monocalcium phosphate*, $Ca(H_2PO_4)_2 + 4C_5H_{11}O_2N,H_3PO_4,4H_2O$; *acid sulphate*, $C_5H_{11}O_2N,H_2SO_4,H_2O$, large, monoclinic prisms, m. p. 80°; *sulphate*, $(C_5H_{11}O_2N)_2,H_2SO_4$, rhombic prisms, m. p. 180°; *basic nitrite*, $(C_5H_{11}O_2N)_2,HNO_2,H_2O$, amorphous, m. p. 220°; *nitrite*, $C_5H_{11}O_2N,HNO_2,H_2O$, rhombic prisms, m. p. 128°; *nitrate*, $C_5H_{11}O_2N,HNO_3$, glittering plates, m. p. 124°; *chlorate*, $C_5H_{11}O_2N,HClO_3$, monoclinic prisms, m. p. 115°; *dichromate*, $C_5H_{11}O_2N,H_2Cr_2O_7$, red crystals, which are turned a deep green on exposure to light, m. p. 226—227° (decomp.); *permanganate*, $C_5H_{11}O_2N,HMnO_4$, violet prisms, m. p. 120°. The latter compound, and the chlorate, readily explode on being rapidly heated or struck.

H. W. B.

Methylenediamine. PETER KNUDSEN (*Ber.*, 1914, **47**, 2698—2701).—Methylenediamine is so unstable that although a few derivatives such as the dibenzoyl compound have been described, the base has not been obtained in a free state or in the form of salts. It has now been discovered that diformomethylenediamide on hydrolysis in the cold with mineral acid gives rise to this base and that various salts can be obtained. Other methylenediamides appear unsuited for this purpose.

Diformomethylenediamide, $CH_2(NH\cdot COH)_2$, was prepared by heating together 60 grams of trioxymethylene and 180 grams of formamide for 4—5 hours under reflux condenser, when a yield of 77 grams was produced. Hydrolysis of this by concentrated hydrochloric acid gave rise to 57 grams of *methylenediamine dihydrochloride*, colourless, hygroscopic prisms. In a similar manner by hydrolysis with nitric acid, the *nitrate* was obtained in prismatic crystals which on heating melt and then explode; the *sulphate*, consisting of small crystals, was obtained by hydrolysis with sulphuric acid of 50% concentration. It was not found possible to isolate the free base, although solutions in such solvents as alcohol are fairly stable and have an ammoniacal odour. The hydrochloride decomposes rapidly in aqueous solution producing formaldehyde; when heated with formaldehyde solution the hydrochloride reacts, forming methylamine hydrochloride and carbon dioxide. Sodium nitrite acts on the aqueous solution of the hydrochloride, giving rise to trinitrosotrimethylenetriamine together with other substances poorer in nitrogen.

Diacetomethylenediamide appears to have its nitrogen less strongly linked, to the methylene radicle, for it does not give methylenediamine but formaldehyde, acetic acid and ammonia on hydrolysis by acids. A similar difference is noted in the behaviour towards benzoylation, for whereas diformomethylenediamide gives rise to dibenzomethylenediamide, diacetomethylenediamide undergoes complete disruption, producing methylene dibenzoate.

D. F. T.

The Plöchl Reaction between Formaldehyde and Ammonia. PETER KNUDSEN (*Ber.*, 1914, **47**, 2694—2698).—The reaction between formaldehyde and ammonia or amines discovered by Plöchl

(A., 1888, 1051) is known to lend itself to the preparation of trimethylamine (Eschweiler, A., 1905, i, 328; Koeppen, A., 1905, i, 328) and of methylamine (Brochet and Cambier, A., 1895, i, 325). The author has now found that it can supply a useful method for the preparation also of dimethylamine by distillation of a solution of ammonium chloride in a sufficient excess of formaldehyde solution under ordinary pressure; the distillate from 100 grams of ammonium chloride and 1000 grams of 40% formaldehyde solution contained 5·7 grams of ammonium chloride with 11·3, 66·1 and 44·4 grams respectively of the hydrochlorides of methylamine, dimethylamine and trimethylamine.

The preparation of the alkylamines as above is effected in heated solutions and is accompanied by the evolution of carbon dioxide. If, however, the reagents are mixed in cold or slightly warmed solution, chemical change occurs, although no carbon dioxide is liberated; formic acid is produced in the solution together with *dimethylpentamethylenetetramine*, $C_5H_{10}N_2(NMe)_2$, which can be separated as the picrate. The formation of the substance, which is a fairly strong monacid base (*picrate*, brown, microscopic crystals, m. p. approximately 195° with decomp.; *mercurichloride*, crystalline powder; *hydrochloride*, leaflets, decomp. 205—206°; *hydrogen carbonate*), is explained by the primary formation of methylamine, as expressed by the equation $2CH_2O + NH_3 = CH_3{\cdot}NH_2 + H{\cdot}CO_2H$, followed by immediate condensation of the methylamine with the excess of formaldehyde. The hydrochloride of dimethylpentamethylenetetramine can also be obtained by the interaction of hexamethylenetetramine, hydrochloric acid and methylamine hydrochloride, neutralising the resulting solution and evaporating. The new base is unstable both towards acids and bases, and its salts with strong acids decompose when warmed in aqueous solution. D. F. T.

*iso*Valine [α-Amino-α-methylbutyric Acid]: Theory of Racemisation. J. Gadamer [with Ernst Rukop] (*J. pr. Chem.*, 1914, [ii], **90**, 405—412).—The author has prepared *dl*-α-amino-α-methylbutyric acid by Ehrlich's method (A., 1908, i, 268) and converted it into its formyl derivative, $C_6H_{11}O_3N$, m. p. 167° (uncorr.), (compare Fischer and von Grävenitz, A., 1914, i, 1057). This was then separated into its active components by means of the quinine salts. *d*-α-Formylamino-α-methylbutyric acid, $[\alpha]_D^{18} - 7{\cdot}2°$, thus obtained yields *d*-α-amino-α-methylbutyric acid, $[\alpha]_D^{20} + 10{\cdot}75°$, this rotation being in good agreement with the value, +11·0°, found by Fischer and von Grävenitz (*loc. cit.*). The *l*-isomeride was not obtained pure, the highest specific rotation obtained being −7·9°. The action of nitrous acid on *l*-α-amino-α-methylbutyric acid yields a small proportion of a dextrorotatory acid, the nature of which was not determined. The *d*-acid undergoes no racemisation when heated with barium hydroxide solution or hydrochloric acid at about 160°. T. H. P.

Aminoalkylcrotonic Acid Nitriles and Monoalkylacetoacetic Acid Nitriles. Ernst Mohr (*J. pr. Chem.*, 1914, [ii], **90**, 189—222).—The aminoalkylcrotonic acid nitriles of the general formula

$$NH_2{\cdot}CMe{:}CR'{\cdot}CN$$

were obtained by the action of methyl, ethyl, *n*-propyl, allyl, and benzyl haloids on sodioacetoacetonitrile. Various methods of procedure were tried, but the reaction seldom proceeded smoothly with the exclusion of by-products, and only in the case of aminomethylcrotononitrile was a crystalline product obtainable. In other cases the crude product was at once saponified by shaking at ordinary temperatures with either dilute sulphuric or concentrated hydrochloric acid for five to ten minutes. The alkyl acetoacetonitrile thus produced was extracted with ether and purified by fractionation in a vacuum. The yields were rarely more than 30% of the theoretical. In carrying out the initial condensation the bromo- or iodo-compounds were in most cases allowed to act directly in benzene or ethereal solution on the mixture of sodium cyanide and sodiodiacetonitrile produced by the action of sodium on acetonitrile, boiling towards the end under a reflux to complete the reaction, and fractionating the product under reduced pressure. A second method adopted varied from the above in that diacetonitrile was first isolated from the mixed sodium salts, and then either a suspension in benzene, or a solution in alcohol, of its sodium salt was treated with the halogen compound as before.

Aminomethylcrotononitrile forms white needles or short prisms, m. p. 122—125°, b. p. 147°/14 mm.

Methylacetoacetonitrile, prepared by the hydrolysis of the above, is a colourless or pale yellow liquid, b. p. 78°/19 mm., 182—184°/745 mm., $D_4^{20} = 0{\cdot}9769$, $n_D = 1{\cdot}4238$. With ammonia the aminonitrile is regenerated; with diethylamine and piperidine no products could be obtained. Semicarbazone, m. p. 153°.

Ethylacetoacetonitrile was prepared by the hydrolysis of crude *aminoethylcrotononitrile*, which could only be obtained as a yellowish-brown oil. It is a colourless or pure yellow liquid, b. p. 84°/16 mm., $D^{19} = 0{\cdot}9555$. It gives metallic derivatives, is very resistant to boiling dilute sulphuric acid, but completely hydrolysed by 33% potassium hydroxide. The semicarbazone melts at 160°.

n-*Propylacetoacetonitrile*, similarly obtained by the hydrolysis of the corresponding impure aminocrotononitrile, is a colourless liquid, b. p. 100°/17 mm., $n_D^{25} = 1{\cdot}4310$—$1{\cdot}4313$. Semicarbazone, m. p. 166°.

Allylacetoacetonitrile produced by the hydrolysis of *aminoallylcrotononitrile*, obtained as an impure dark red oil, is a yellow oil, b. p. 91—93°/11 mm., $n_D^{18} = 1{\cdot}4545$. Semicarbazone, m. p. 159°.

Benzylacetoacetonitrile was obtained by the hydrolysis of the impure *aminobenzylcrotononitrile*. It was never obtained in an analytically pure condition. The purest samples obtained had $D^{20} = 1{\cdot}0712$, $n_D = 1{\cdot}526$—$1{\cdot}528$, b. p. about 159°/12 mm. *Semicarbazone*, m. p. 168°. With hydroxylamine, white needles, m. p. 76°, were obtained, but whether they were the oxime or an *iso*oxazole derivative was not determined. G. F. M.

The Course of the Action of Ammonia and Carbamide on Esters of Unsaturated Acids. III. ERNST PHILIPPI and EMIL SPENNER (*Monatsh.*, 1915, **36**, 97—111).—The authors have examined the behaviour of unsaturated esters towards ammonia and

carbamide in order to determine whether addition at the unsaturated linking has precedence over the formation of an amide, and also to learn the influence of substituents on the addition. They find that, in general, the addition takes place readily and that the amino-group attaches itself to the carbon atom remote from the ester group. Negative substituents and benzene nuclei hinder the addition, and an amino- or carbamido-group already attached to a doubly-linked carbon atom entirely prevents the further addition of a like group. The presence of a double bond in the $\alpha\beta$ position with respect to an ester group greatly hinders the formation of an amide, and, if this reaction sets in at all, it is after addition to the unsaturated linking has taken place (compare ethyl fumarate and ethyl acrylate).

The reaction with ethyl itaconate, $CO_2Et\cdot CH_2\cdot C(CO_2Et):CH_2$, should have given interesting results because one ester group is in the critical $\alpha\beta$-position, whilst the other is more remote from the ethylene linking. Unfortunately, the product was a mixture which could not be separated.

For the first time, the reaction of an acetylenic ester, namely, ethyl phenylpropiolate, with ammonia or carbamide has been examined. The result is somewhat surprising, for phenylpropiolamide is formed in good yield at the room temperature, but ammonia is attached to the unsaturated linking at 100°, giving an ethyl aminocinnamate. This is probably a β-amino-derivative, but it is not certain. Carbamide, at 150°, gives a better yield of the aminocinnamate than does ammonia. This is because a certain amount of the amide is formed by ammonia during the time required to seal the tube and raise it to 100°, whereas carbamide only begins to provide ammonia at the higher temperature.

This addition of ammonia offers the best method for the preparation of many β-amino-acids and esters.

Ethyl acrylate, when heated with carbamide and alcohol at 140°, yielded dihydrouracil, and ethyl crotonate yielded methyldihydrouracil (E. Fischer and Röder, A., 1901, i, 295). The latter ester gave a 75% yield of ethyl β-aminobutyrate with alcoholic ammonia at 110°. Ethyl carbamidocrotonate was heated with alcoholic carbamide for several hours at 150°, but only a 30% yield of *ethyl β-amino-β-carbamidobutyrate*, $NH_2\cdot CO\cdot NH\cdot CMe(NH_2)\cdot CH_2\cdot CO_2Et$, m. p. 130—131°, was obtained. Ethyl citraconate was left with liquid ammonia, when a small quantity of an *ethyl aminomethylsuccinate*, $C_9H_{17}O_4N$, b. p. 225°/10 mm, and a trace of citraconamide were formed. Ethyl cinnamate and ethyl diphenylitaconate were unaffected by ammonia or carbamide.

Ethyl phenylpropiolate was prepared most conveniently and in good yield by Perkin's method. The *ethyl aminocinnamate* which this ester yielded when heated with ammonia or carbamide had b. p. 170°/10 mm., was very sensitive towards acids, and gave benzoic acid and ethyl phenylpropiolate when treated with nitrous fumes. J. C. W.

Carbethoxyaminoacetaldehyde. C. Harries and Friedrich Düvel (*Ber.*, 1914, **47**, 3344—3346).—Allylurethane is ozonised in glacial acetic acid solution. The *ozonide* is decomposed by heating on the water-bath and the solvent removed under diminished pressure.

The distillate contains formaldehyde and formic acid; the residue yields two fractions on distillation. The first of these, b. p. 79—80°/0·5 mm., is *carbethoxyaminoacetaldehyde*, $CO_2Et\cdot NH\cdot CH_2\cdot CHO$, which forms a colourless oil resembling glycerol, shows strong reducing action, and has $D_4^{21\cdot5}$ 1·1484, $n_D^{21\cdot5}$ 1·44221, n_α 1·43970, n_β 1·44866, n_γ 1·45371. Attempts to prepare a crystalline oxime, semicarbazone or phenylhydrazone were unsuccessful, but *p*-nitrophenylhydrazine gave a yellowish-brown *hydrazone*, $C_{11}H_{14}O_4N_4$, which did not melt below 270°.

The second fraction, b. p. 90—140°/0·5 mm., became partly crystalline and appeared to consist of a polymerisation product of the above substance, which still retained aldehydic nature.

Carbomethoxyaminoaldehyde could not be prepared in a similar manner, methylurethane being identified among the products of fission.

H. W.

The Action of Primary Amines on Substances which Yield 1 : 3-Diketones. L. Rügheimer (*Ber.*, 1914, **47**, 2759—2765).—Methyl β-benzyliminopropyl ketone, obtained by the condensation of benzylamine with acetylacetone (Rügheimer and Ritter, A., 1912, i, 474), appears to consist, at least for the greater part, of the enolic form, $CH_2Ph\cdot N{:}CMe\cdot CH{:}CMe\cdot OH$. Analogous compounds derived from aliphatic amines have now been examined, and the results as to the enolic or ketonic condition of the substances do not altogether agree with those of the original investigators of these substances (Combes and Combes, A., 1893, i, 454), who regarded methyl β-ethyliminopropyl ketone as of ketonic structure, whereas its alcoholic solution gives a colour reaction with ferric chloride, and the oily benzoyl derivative by its easy hydrolysis suggests an *O*-derivative; the p-*nitrobenzoyl* derivative, tablets, m. p. 92°, was also prepared.

For the primary alkylamine derivatives of βδ-diketo-γ-methyl-*n*-pentane (methylacetylacetone), to which feeble acidic properties were ascribed earlier, the author claims that only basic properties are present.

The enolisation of compounds of this type is believed to be favoured by the basicity of the alkylimino-radicle, and evidence of this is produced in the almost entire absence of ferric chloride coloration with the dihydrochloride of ββ-ethylenedi-iminodipropyl methyl ketone, $CH_2Ac\cdot CMe{:}N\cdot CH_2\cdot CH_2\cdot N{:}CMe\cdot CH_2Ac$, whereas the free base readily gives such a coloration.

A suggestion is made that the formation of these condensation products depends on a primary addition of the base to the enolic form of the diketone, the resulting compound of the type

$$NHR\cdot CMe(OH)\cdot CH_2\cdot CO\cdot CH_3$$

undergoing subsequent elimination of the elements of water.

D. F. T.

A New Method for the Preparation of Secondary Amides. Karl Brunner (*Ber.*, 1914, **47**, 2671—2680).—It has been discovered that acetic anhydride will react with potassium cyanate producing diacetamide, this result recalling the production of diacetoethylamide

from ethylcarbimide and acetic anhydride by Wurtz in 1854. With the potassium cyanate, however, the reaction occurs much more readily, needing no application of heat, and the acetic anhydride can conveniently be diluted with benzene or ether. Contrary to expectation, the new reaction is not strictly analogous to that examined by Wurtz, for the results indicate that instead of equimolecular proportions being involved as in the change

$$CN\cdot OEt + Ac_2O = CO_2 + NAc_2Et,$$

the relative quantity of the reagents is expressed by the equation $KCNO + 2Ac_2O = C_6H_9O_3N + CO_2 + AcOK$, an equation similar to that with ethylcarbimide, representing an intermediate stage in the process. The nitrogen product in the equation is not triacetamide, although agreeing with this in composition; the new *substance*, $C_6H_9O_3N$, was with considerable difficulty isolated, and found to form a colourless liquid, b. p. 86—90°/11 mm., solidifying to rectangular leaflets, m. p. 7—8°: it readily undergoes decomposition, and when heated under ordinary pressure fails to distil, actually yielding diacetamide and a carbonaceous residue. Diacetamide is also produced when the new substance is exposed to the atmosphere for a short time, atmospheric moisture being the probable agent, and it is therefore hardly surprising that in the absence of special precautions, diacetamide is the usual product of the interaction of potassium cyanate and acetic anhydride. It is probable that the new substance, for which the structure OAc·CMe:NAc is suggested, is identical with a substance of similar composition and volatility obtained by the action of acetic anhydride on sodium diacetamide (Hentschel, A., 1890, 1239).

An endeavour to obtain diacetamide as a primary product of such a reaction by using cyanic acid in place of the potassium salt gave no trace of the desired substance. On the other hand, acetic anhydride can be replaced by homologous compounds, propionic, butyric and *iso*butyric anhydrides giving rise to secondary amides in good yield, but with benzoic anhydride the yield of dibenzamide was very poor, small quantities of tribenzamide and benzonitrile also being obtained. Potassium thiocyanate exhibits similar behaviour to the cyanate towards acetic anhydride, giving diacetamide.

Semicarbazide hydrochloride is found to act as a convenient reagent for distinguishing secondary amides from primary. With the latter class of compound no appreciable change is obtained in aqueous solution with this substance to which a little potassium acetate has been added, whereas diacetamide under these conditions gives a deposit of hydrazoformamide. D. F. T.

Action of Sulphides on Nitroprussides, and the Nature of the Coloured Substances Produced. José Giral Pereira (*Anal. Fis. Quim.*, 1915, **13**, 27—46, 69—82).—Solutions of sodium nitroprusside and sodium sulphide in metanol yield a violet precipitate, which is very hygroscopic and readily oxidised by air. With potassium sulphide an analogous derivative is produced, the reaction corresponding with the equation

$$(CN)_5Fe(NO)Na_2,2H_2O + 2K_2S = (CN)_5FeNa_2K_4S_2,2H_2O + NO.$$

A. J. W.

Removal of Oxygen from Triethylphosphine Oxide. J. N. COLLIE and F. REYNOLDS (T., 1915, **107**, 367—369).—*Triethylphosphine oxide*, prepared by boiling triethylphosphine with concentrated nitric acid, is extremely stable, and cannot be made to part with its oxygen by treatment with sodium, zinc, or magnesium even at high temperatures. It reacts, however, with phosphorus pentachloride to give *triethylphosphine dichloride*, PEt_3Cl_2, a crystalline substance which is reduced in alcoholic solution by sodium amalgam to triethylphosphine. With water it was reconverted into the oxide. When distilled, much decomposition occurred and ethyl chloride and other inflammable gases were evolved, whilst the distillate contained triethylphosphine hydrochloride and *monochlorodiethylphosphine*, the latter formed according to the equation $PEt_3Cl_2 = PEt_2Cl + EtCl$. It was detected by conversion into diethylphosphinic acid, PEt_2O_2H, by treatment with water and nitric acid, and this was isolated as its silver salt by boiling with water and silver oxide, filtering, and evaporating the filtrate to crystallisation. G. F. M.

Researches on Silicon Compounds. VIII. Preparation and Constitution of Silico-oxalic Acids, and the Action of Methyl and Ethyl Alcohols on Trisilicon Octachloride. GEOFFREY MARTIN (T., 1915, **107**, 319—328).—The methods hitherto described for the preparation of silico-oxalic acid do not yield the compound in a state of purity. It has now been found that almost pure silico-oxalic acid can be obtained in nearly quantitative yield by the action of cold water on hexaethoxysilicoethane. If hot water is used, the product is less pure. Pure silico-oxalic acid is a white, amorphous powder; it is decomposed by alkali hydroxide with evolution of hydrogen, and undergoes explosive decomposition when submitted to pressure, friction, or sudden heating.

In view of the success obtained by this method of preparing silico-oxalic acid, experiments were made to obtain mesosilico-oxalic acid, $HO_2Si{\cdot}Si(OH)_2{\cdot}SiO_2H$, by preparing octaethoxysilicopropane, $Si_3(OEt)_8$, and decomposing it with water. It was found, however, that when trisilicon octachloride is treated with alcohol, octaethoxysilicopropane is not obtained, but decomposition takes place with formation of tetraethoxysilicomethane and other products. A similar attempt was made to prepare octamethoxysilicopropane, $Si_3(OMe)_8$, by the action of methyl alcohol on trisilicon octachloride, but without success.

Experiments are described which indicate that mesosilico-oxalic acid is less stable than silico-oxalic acid.

The constitution of silico-oxalic acid is discussed, and it is shown that it may be represented by the formula HO·SiO·SiO·OH unless perchance it is a cyclic compound. E. G.

Action of Salts of the Heavy Metals on Organo-magnesium Compounds. N. V. KONDYREV and D. A. FOMIN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 190—198).—With organo-magnesium compounds, various salts of the heavy metals react with extreme energy, thermal effects, change of colour and complete resolution of the organo-

magnesium compound taking place. Further, when such a salt is added to an ethereal solution of an organo-magnesium compound, or when an ethereal solution of an alkyl haloid is added to a mixture of the salt with magnesium, the resulting products comprise hydrocarbons formed by the decomposition of the organo-magnesium derivative and magnesium haloid, the salt being at the same time reduced, in some instances to metal. The decomposition of the organo-magnesium compound leads to the formation of the saturated and unsaturated hydrocarbons corresponding with the alkyl group present; thus, magnesium ethyl haloid gives ethane and ethylene and magnesium propyl haloid, propane and propylene. When a magnesium aryl haloid is used, two aryl radicles unite, magnesium phenyl haloid yielding diphenyl, and magnesium tolyl haloid, ditolyl. The quantitative character of these decompositions, their occurrence at low temperatures and the simplicity of the necessary manipulation render this method of obtaining hydrocarbons especially suitable in cases where the ordinary method of removing hydrogen haloid is impracticable. The salts employed in the investigations were cuprous chloride, bromide, iodide, cyanide and thiocyanate, cupric bromide, ferrous, ferric, cobalt and nickel chlorides, and ferric, chromic and molybdenum thiocyanates.

Together with unsaturated hydrocarbon, the action of chloral or of benzophenone on magnesium ethyl bromide yields also ethane (compare Iocitsch, A., 1914, i, 375). T. H. P.

Action of Anhydrous Aluminium Chloride and Trioxymethylene on *cyclo*Hexane. A. M. Nastjukov and N. V. Gurin (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 46—52).—Experiments with *cyclo*hexane show that, when heated with anhydrous aluminium chloride and trioxymethylene, naphthenes yield condensation products possessing the characters of saturated and unsaturated hydrocarbons, just as is the case with olefines (compare Aschan, A., 1902, i, 749; Engler, with Routala, A., 1910, i, 2, 160, and, with Halmai, A., 1910, i, 160) and terpenes (compare Steinkopf and Freund, A., 1914, i, 304). This reaction, which occurs also with heptane and octane, but not with pentane or hexane, is a complex one, dehydrogenation being accompanied by condensation; as a result of the latter process soluble formolites are formed (compare Nastjukov and Maljarov, A., 1911, i, 249).

T. H. P.

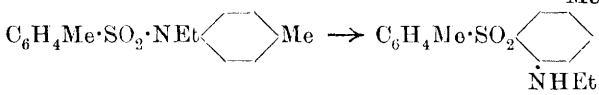
Polymerisation and Depolymerisation in Solutions. Hans Stobbe (*Ber.*, 1914, **47**, 2701—2703).—The fact that the spontaneous change from styrene to metastyrene appears never to be complete leads to the view that the final state is one of equilibrium, and the author has examined solutions of styrene and of metastyrene in benzene.

[With Fritz Reuss and Alfred Lippold.]—Benzene solutions of styrene and metastyrene undergo no change in the dark, but on exposure to sunlight the refractive index of the styrene solution gradually rises, whilst that of the metastyrene solution gradually falls,

thus indicating the tendency to attain the same equilibrium mixture. The presence of metastyrene and styrene respectively in the two solutions could be readily detected after the illumination.

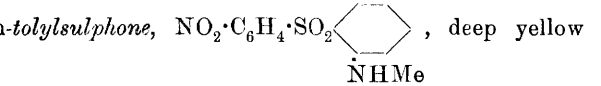
[With FRITZ DÜNNHAUPT.]—The formation of distilbene from stilbene in benzene solution (Ciamician and Silber, A., 1903, i, 171) can be detected by change in the refractive index already after three days' illumination. No indication could be obtained, however, of the reverse change in a solution of distilbene in benzene, nor, indeed, could any alteration be observed even with stilbene solutions in alcohol, ether, chloroform, trichloroethylene or pyridine. D. F. T.

Rearrangements with Arylamides of *m*-Nitrobenzenesulphonic Acid. OTTO N. WITT and H. TRUTTWIN (*Ber.*, 1914, **47**, 2786—2795).—The rearrangement produced in *p*-toluenesulphonethyl-*p*-toluidide with formation of *o*-ethylamino-*mp*-ditolylsulphone according to the scheme



(Witt and Uerményi, A., 1913, i, 350) under the influence of sulphuric acid also occurs with the methyl derivative of the condensation product of *m*-nitrobenzenesulphonyl chloride and *p*-toluidine.

m-*Nitrobenzenesulpho*-p-*toluidide*, $NO_2 \cdot C_6H_4 \cdot SO_2 \cdot NH \cdot C_6H_4Me$, rhombohedral crystals, m. p. 130·5° (corr.), is converted by methyl sulphate and sodium hydroxide solution into m-*nitrobenzenesulphomethyl*-p-*toluidide*, $NO_2 \cdot C_6H_4 \cdot SO_2 \cdot NMe \cdot C_6H_4Me$, m. p. 104°, which when heated at 100° for a short time with concentrated sulphuric acid undergoes intramolecular rearrangement into m-*nitrophenyl*-o-*methyl*-

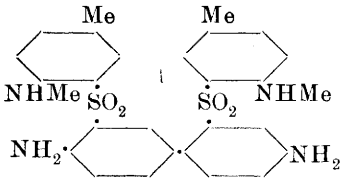


amino-m-*tolylsulphone*, , deep yellow crystals, m. p. 148·5°; this rearrangement affects approximately 83% of the compound, only 17% undergoing hydrolysis. The *acetyl* derivative of this methylaminosulphone could not be obtained crystalline.

Reduction of *m*-nitrophenyl-*o*-methylamino-*m*-tolylsulphone by stannous chloride in hydrochloric acid solution yielded m-*aminophenyl*-o-*methylamino*-m-*tolylsulphone*, $NH_2 \cdot C_6H_4 \cdot SO_2 \cdot C_6H_3Me \cdot NHMe$, m. p. 150° (*acetyl* derivative, $NHAc \cdot C_6H_4 \cdot SO_2 \cdot C_6H_3Me \cdot NHMe$, prisms, m. p. 170°), which when diazotised and coupled with sodium β-naphthol-3 : 6-disulphonate (*R*-salt) gave an orange-red azo-dye.

On the other hand, reduction by alkaline agents such as sodium methoxide produces m-*azoxyphenyl*-o-*methylamino*-m-*tolylsulphone*, $ON_2(C_6H_4 \cdot SO_2 \cdot C_6H_3Me \cdot NHMe)_2$, m. p. 330°, soluble in sulphuric acid to a blue colour. Sodium methoxide also reduces the original *m*-nitrobenzenesulpho-*p*-toluidide to an *azoxy*-derivative. Further reduction of the former azoxy-compound did not give rise to the amino-compound obtained by acid reduction; the action of stannous

chloride in acetic acid solution effected gradual reduction with concurrent benzidine rearrangement with formation of *o-dimethylamino-di-*m*-tolylbenzidine-2 : 2′-disulphone* (annexed formula), m. p. 213°, which gives a violet dye with *R*-salt. By boiling the tetrazo-solution obtainable from the benzidine compound with alcohol and copper sulphate, the diazo-groups can be eliminated with formation of *di-*o*-methylamino-*m*-ditolyl-2 : 2′-diphenyldisulphone*, $C_{12}H_8(SO_2 \cdot C_6H_3Me \cdot NHMe)_2$, m. p. 154°.



In an endeavour to synthesise the last-named substance by an independent method, potassium *m*-nitrobenzenesulphonate was converted through azobenzene-*m*-disulphonic acid into benzidine-*m*-disulphonic acid. The tetrazo-derivative of the last compound by treatment with alcohol and copper powder was converted into diphenyldisulphonic acid, the dichloride of which was found to melt at 142°; condensation of this with *p*-toluidine yielded *diphenyldisulpho-*p*-toluidide*, an amorphous solid, m. p. 87°, which gives a *potassium* salt. Methylation of the toluidide by methyl sulphate produced *diphenyldisulphomethyl-*p*-toluidide*, m. p. 145·5°, which under the action of sulphuric acid underwent the desired rearrangement, but simultaneously underwent scission of methyl-*p*-toluidinesulphonic acid, the isolated product being *o-methylamino-*m*-tolyldiphenylsulphone*,

$$C_6H_5 \cdot C_6H_4 \cdot SO_2 \cdot C_6H_3Me \cdot NHMe,$$

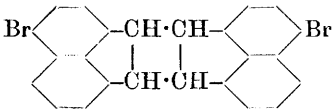
colourless crystals, m. p. 215·5°. D. F. T.

Stereoisomerism of *s*-Diphenyldiethylethane [γδ-Diphenylhexane]. A. I. Ljepin and V. N. Reich (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 149—160. Compare A., 1912, i, 958).—Conversion of phenylethylcarbinol into the corresponding bromide and treatment of the latter, in benzene solution, with sodium yields, together with α-phenylpropylene, a polymeride of it, and propylbenzene, two isomeric *γδ-diphenylhexanes*, CHPhEt·CHPhEt : (1) a viscous, fluorescent liquid, b. p. 297—298°/767 mm., D_4^0 0·9742, D_4^{20} 0·9591, n_D^{20} 1·54622, which has a pleasant odour, exhibits normal cryoscopic behaviour in benzene and solidifies to a glassy mass when cooled in ether and solid carbon dioxide; (2) a crystalline solid, m. p. 90°, b. p. 304—305°/767 mm., which has the normal molecular weight in freezing benzene. Both of these isomerides are quite stable at their boiling points and, when oxidised with chromium trioxide, potassium hydrogen sulphate and acetic acid (compare Willstätter, Mayer and Hüni, A., 1911, i, 144), both yield phenyl ethyl ketone. Each undergoes partial isomerisation into the other when heated in a sealed tube with a small proportion of iodine at 250—265°. The liquid form is probably a mixture of the *d*- and *l*-antipodes, and the solid, the internally compensated compound. T. H. P.

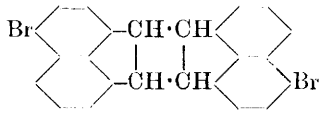
The Heptacyclenes. Diacenaphthyl (Dinaphthylenebutane), a New Hydrocarbon. K. Dziewónski and C. Paschalski (*Ber.*, 1914, **47**, 2680—2686).—In an endeavour to pursue further the

examination of the *cis-trans* isomerism of the two heptacyclenes (A., 1913, i, 847) obtained from acenaphthylene by the action of sunlight, the authors have submitted these two hydrocarbons to bromination, nitration and reduction.

Each of the heptacyclenes on treatment with a bimolecular proportion of bromine in chloroform solution yields two dibromides of the formula $C_{24}H_{14}Br_2$, all of which compounds undergo quantitative oxidation by chromic acid with production of α-bromonaphthalic anhydride, thus indicating the relative formulæ I and II for the two dibromides of each hydrocarbon:



(I.)

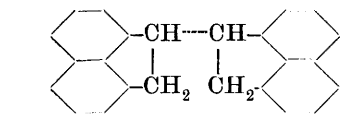


(II.)

The two *αα'-dibromides* derived from α-heptacyclene form silky needles, m. p. 303—304°, and microscopic needles, m. p. 274—275°, respectively; the latter compound gives an orange-yellow *picrate*, needles, m. p. 218°. The *αα'-dibromides* from β-heptacyclene form colourless prisms, m. p. 267°, and tablets, m. p. 212°, respectively, the latter giving a *picrate*, red prisms, m. p. 180°.

α-Heptacyclene is remarkably resistant to nitration and is hardly affected, but the β-isomeride yields two isomeric *dinitro-β-heptacyclenes*, needles, m. p. 306°, and cubes, m. p. 282°, respectively.

Both heptacyclenes were reducible by hydriodic acid and red phosphorus under increased pressure at 185—190° and 220—230° for the β- and α-isomerides respectively, the product being *diacenaphthyl* or *dinaphthylenebutane* (formula III), the formation of which provides confirmatory evidence of the geometrical isomerism of the parent hydrocarbons. The new hydrocarbon forms hexagonal tablets, m. p. 120°; *picrate*, yellow needles, m. p. 222°.



(III.)

D. F. T.

Bromination of Aniline. Hartwig Franzen and Alfred Henglein (*J. pr. Chem.*, 1915, [ii], **91**, 245—257).—The authors have applied the method used in the preparation of 1 : 6-dibromo-2-naphthylamine (A., 1914, i, 162) to the benzene series. It was shown by Hantzsch (A., 1891, 50) that benzylideneaniline dibromide is decomposed into *p*-bromoaniline and benzaldehyde under the influence of many substances, an alcoholic solution of sodium ethoxide and pyridine giving good results in this respect. When this dibromide is heated with a little absolute alcohol and subsequently cooled, a considerable amount of benzylidene-*p*-bromoaniline hydrobromide,

$$C_6H_4Br\cdot N{:}CHPh,HBr,$$

and not unaltered benzylideneaniline dibromide, as Hantzsch supposed, separates. Contrary to the opinion of Hantzsch and Schwab (A., 1901, i, 378), the authors consider that in benzylideneaniline hydro-

bromide the hydrogen bromide is not combined as in salts, but that its formation from benzylideneaniline dibromide may be represented thus:

$$\begin{matrix} C_6H_5\cdot N\text{–}CHPh \\ \dot{B}r\ \dot{B}r \end{matrix} \longrightarrow C_6H_4Br\cdot NH\cdot CHPhBr,$$

the reaction being similar to $NPhClAc \longrightarrow C_6H_4Cl\cdot NHAc$. The action of pyridine on benzylideneaniline dibromide gives benzylidene-*p*-bromoaniline in good yield; this change is analogous to that just considered, the benzylidene-*p*-bromoaniline hydrobromide formed being unstable under the conditions employed and decomposing into hydrogen bromide and benzylidene-*p*-bromoaniline. Here, also, when *p*-bromoaniline is to be prepared, the isolation of the intermediate products is unnecessary, but the product is mixed with 2 : 4-dibromoaniline.

By converting benzylidene-*p*-bromoaniline into its dibromide and boiling this with alcohol, benzylidene-2 : 4-dibromoaniline hydrobromide is obtained. The action of pyridine on the dibromide does not result in the separation of benzylidene-2 : 4-dibromoaniline, which is extremely difficult to crystallise, but treatment of the products of the reaction with hot dilute sulphuric acid gives 2 : 4-dibromoaniline mixed with a considerable proportion of 2 : 4 : 6-tribromoaniline; the former goes into solution as sulphate, whilst the latter remains undissolved. The preparation of 2 : 4-dibromoaniline does not necessitate the isolation of pure *p*-bromoaniline.

From 2 : 4-dibromoaniline, the benzylidene-compound may be prepared and from this, its dibromide. In this case, however, benzylidene-2 : 4 : 6-tribromoaniline hydrobromide does not result, since it is immediately decomposed with formation of 2 : 4 : 6-tribromoaniline; similar behaviour is shown when the dibromide is treated with pyridine.

Benzylidene-p-*bromoaniline hydrobromide*, $C_6H_4Br\cdot NH\cdot CHPhBr$, forms a pale yellow, crystalline powder, beginning to darken at 160°, m. p. 215° (decomp.). *Benzylidene*-p-*bromoaniline dibromide*, $C_6H_4Br\cdot NBr\cdot CHPhBr$, forms a dark yellow, apparently amorphous powder, m. p. 182° (blackens). *Benzylidene*-2 : 4-*dibromoaniline hydrobromide*, $C_6H_3Br_2\cdot NH\cdot CHPhBr$, forms a yellow, crystalline powder. *Benzylidene*-2 : 4-*dibromoaniline*, $C_6H_3Br_2\cdot N{:}CHPh$, forms pale yellow needles, m. p. 67°, and its *dibromide*, $C_6H_3Br_2\cdot NBr\cdot CHPhBr$, slender, orange-yellow needles, m. p. 115—120° (decomp.). T. H. P

Dimethyloxanilide. R. Stolle and M. Luther (*J. pr. Chem.*, 1914, [ii], **90**, 275—276).—Dimethyloxanilide was obtained in quantitative yield by the action of 4 mols. methylaniline on oxalyl chloride (1 mol.). It crystallised in slender needles, m. p. 110°. The statements of Bischoff and Fröhlich (A., 1907, i, 28) and Norton and Livermore (A., 1887, 1083) with regard to this substance should therefore be corrected in the literature. G. F. M.

Preparation of Phenol from Chlorobenzene. Kurt H. Meyer and Friedrich Bergius (*Ber.*, 1914, **47**, 3155—3160).—Dussart and

Bardy in 1872 briefly stated that chlorobenzene is smoothly converted into phenol by the action of sodium hydroxide solution at 300°. This statement, which was not credited at the time, has now been confirmed and the action of water and alkalis on aromatic haloids submitted to a general examination.

When chlorobenzene is heated for some hours with water at 300°, a trace of phenol is formed, but when the vapour mixed with steam is passed through tubes, with or without catalysts, at 600—700°, most of the chlorobenzene suffers decomposition into tarry products.

The best results are obtained with 15 to 20% sodium hydroxide in high pressure autoclaves. It seems that the sodium phenoxide which is first formed quickly reacts with more chlorobenzene to form phenyl ether, which is only hydrolysed by long contact with a considerable excess of the alkali. Thus, with 4 molecular proportions of sodium hydroxide, and twenty hours' heating at 300°, a 96% yield of phenol is obtained, in a pure white condition. With less alkali, a certain amount of ether is formed. Concentrated alkali has no action in stationary autoclaves, but produces hydrogen and naphthalene in rotated autoclaves. Other bases have hardly any action.

Bromobenzene, chlorotoluene, and α-chloronaphthalene were also converted into the corresponding phenols by this means. J. C. W.

Conversion of Aromatic Sulphonic Acids into Phenols. Francis Willson and Kurt H. Meyer. (*Ber.*, 1914, **47**, 3160—3163).—The behaviour of sulphonic acids towards aqueous alkalis at high temperatures and under pressure has been examined.

Benzenesulphonic acid is slowly attacked by 10% sodium hydroxide at 320°, but the naphthalenesulphonic acids readily give good yields of the very pure naphthols. Benzenedisulphonic acid, instead of yielding resorcinol, can only be hydrolysed to *m*-phenolsulphonic acid. *o*- and *p*-Phenolsulphonic acids give free phenol and only minute traces of the dihydroxybenzenes. It seems, therefore, that the scission into the phenol and the sulphite is accompanied by the competing reaction, the scission into the hydrocarbon and the sulphate.

A halogen atom is more readily removed than the sulphonic acid group, for *p*-chlorobenzenesulphonic acid yields *p*-phenolsulphonic acid. Calcium hydroxide or sodium carbonate solutions have little effect. J. C. W.

Orthoformic Esters as Alkylating Agents. R. von Walther (*J. pr. Chem.*, 1914, [ii], **91**, 258—260).—*s*-Trinitrophenetole may be obtained in theoretical yield by heating a mixture of picric acid and ethyl orthoformate in equal proportions in an oil-bath slowly to 170°, and when 2 : 4-dinitrophenol and ethyl orthoformate are heated together directly over the flame, 2 : 4-dinitrophenetole is formed in 50% yield. T. H. P.

Catechol Compounds of Aluminium and of Magnesium, and a Pyrogallol-Iron Compound. R. F. Weinland and Wilhelm Denzel (*Ber.*, 1914, **47**, 2753—2759. Compare A., 1914, i, 953; *Ber.*, 1914, **47**, 2244; also Weinland and Binder, A., 1912, i, 184, 445).—A solution of aluminium acetate, catechol, and potassium acetate in

the molecular proportions 1 : 3 : 9, on evaporation will yield elongated laminæ of a double *compound*, the formula of which is most satisfactorily represented as

$$[Al(C_6H_4O_2)_3]K_2H,[Al(C_6H_4O_2)_2]K,C_6H_4(OH)_2,2HAc,9H_2O.$$

Magnesium can give rise to similar complex compounds, and a solution of magnesium chloride and catechol in the molecular proportions 1 : 2·2, after the addition of 5—10 equivalents of ammonia in aqueous solution, will deposit microscopic tablets of a *compound*, $[Mg(C_6H_4O_2)_2]H_2,1\frac{1}{2}NH_3$, which dissolves in cold water to a clear alkaline solution. If less alkali than that above specified is used, for example, 1—3 molecular proportions of ammonia or even of an alkali hydroxide, a colourless powdery deposit is obtained of a magnesium *compound* of catechol of the composition

$$(C_6H_4O_2H)_2Mg,2\tfrac{1}{2}H_2O.$$

From a solution of ferric acetate, pyrogallol and ammonia in water in the molecular proportions 1 : 3 : 2½, a brownish-black, crystalline deposit is obtainable, which under the microscope appears as reddish-violet, rhombic leaflets, the composition of the *compound* being $[Fe_3(C_6H_3O_3)_5]H_6,(NH_3)_3,6H_2O$. The existence of a violet and also of a blue compound of similar constituents is also reported, but their composition is uncertain. D. F. T.

A Reaction of Homopiperonyl and Homoveratryl Alcohols. (Mrs.) Gertrude Maud Robinson (T., 1915, **107**, 267—276. Compare P., 1914, **30**, 252).—It has been shown in the preliminary paper (*loc. cit.*) that when 2 : 3 : 6 : 7-tetramethoxy-9 : 10-dihydroanthracene is heated with litharge, 2 : 3 : 6 : 7-tetramethoxyanthracene is produced. It was thought that this substance might perhaps be obtainable by an internal condensation of hydroveratroin or by the condensation of veratrole with glyoxal. It has been found that hydroveratroin can be condensed by means of tin chloride, but that the product is tetramethoxydeoxybenzoin. When a mixture of veratrole, glyoxal sodium hydrogen sulphite, and sulphuric acid is warmed for ten minutes on the water-bath and subsequently treated with water, *s-tetraveratrylethane*, $CH[C_6H_3(OMe)_2]_2{\cdot}CH[C_6H_3(OMe)_2]_2$, m. p. 148°, is produced which forms colourless needles; it yields with sulphuric acid a plum-coloured solution which, on addition of water, becomes first green and then pink.

When 3 : 4 : 3′ : 4′-tetramethoxybenzophenone, prepared by a modification of Kostanecki and Tambor's method (A., 1907, i, 75), is reduced with sodium and alcohol, it yields 3 : 4 : 3′ : 4′-*tetramethoxydiphenylmethane*, $C_6H_3(OMe)_2{\cdot}CH_2{\cdot}C_6H_3(OMe)_2$, b. p. 257°/24 mm., m. p. 70°, which crystallises in colourless, glistening leaflets, and when treated with sulphuric acid and formaldehyde is converted into 2 : 3 : 6 : 7-tetramethoxy-9 : 10-dihydroanthracene, identical with that obtained from homoveratryl alcohol (*loc. cit.*).

Attempts were made to prepare a crystalline nitro-derivative from di*iso* afrole, but without success. E. G.

Oxidation of Tetrahydroxydiphenyl to Tartronic Acid. A Correction. O. von Friedrichs (*Ber.*, 1914, **47**, 3369).—The substance previously described as tartronic acid (*ibid.*, 2983) is now

found to be anhydrous oxalic acid, the m. p. and percentage composition of which are practically identical with those of hydrated tartronic acid. H. W.

Aryl Chlorothiols. III. 3-Nitro-4-chlorothioltoluene. Th. Zincke and H. Röse (*Annalen*, 1914, **406**, 103—126. Compare A., 1912, i, 762).—3 : 3′-*Dinitrodi*-p-*tolyl disulphide*, $S_2(C_6H_3Me\cdot NO_2)_2$, yellow needles, m. p. 176°, is prepared from 4-chloro-3-nitrotoluene by Wohlfart's method (A., 1903, i, 203). A by-product of the reaction is 3-*nitro*-3′-*aminodi*-p-*tolyl disulphide*, $C_{14}H_{14}O_2N_2S_2$, golden-yellow needles, m. p. 161°, which forms an *acetyl* derivative, pale yellow needles, m. p. 167°, and is reduced by sodium sulphide in warm alcoholic alkaline solution, yielding 3-nitro- and 3-amino-*p*-tolyl mercaptans, which are identified in the form of their methyl derivatives (following abstract).

By treatment with chlorine or bromine the dinitroditolyl disulphide, when suspended in glacial acetic acid, yields the sulphonyl chloride, m. p. 98—99°, or sulphonyl bromide, m. p. 115° (following abstract), but when suspended in carbon tetrachloride the product is 3-*nitro*-4-*chlorothioltoluene*, $NO_2\cdot C_6H_3Me\cdot SCl$, yellow needles, m. p. 90°, or 3-*nitro*-4-*bromothioltoluene*, orange-yellow needles, m. p. 95°. The halogen atom in these two substances is very reactive, the substances closely resembling 2-nitro-1-chlorothiolbenzene (*loc. cit.*) in their behaviour. 3-Nitro-4-chlorothioltoluene is converted into the dinitrodi-*p*-tolyl disulphide and *m*-toluidine-4-sulphonic acid by boiling aqueous methyl alcohol, and into 3-*nitro*-p-*tolyl thiocyanate*, $NO_2\cdot C_6H_3Me\cdot SCN$, yellow needles, m. p. 125°, by the action of potassium cyanide in a boiling mixture of chloroform and glacial acetic acid. It is converted into 3-*nitro*-4-*methoxythioltoluene*, $NO_2\cdot C_6H_3Me\cdot S\cdot OMe$, dark yellow crystals, m. p. 71°, by sodium methoxide suspended in ether, and reacts slowly with water to form the *oxide*, $(NO_2\cdot C_6H_3Me\cdot S)_2O$, pale yellow crystalline powder, m. p. 194° with previous blackening. The latter in the presence of alcohol reacts with alkali hydroxides and with ammonia to form deep blue solutions of the unstable salts of the unknown hydroxythiol, $NO_2\cdot C_6H_3Me\cdot S\cdot OH$, which decompose by keeping, yielding the dinitrodi-*p*-tolyl disulphide and 3-nitro-*p*-toluenesulphinic acid (see below).

3 : 3′-*Dinitrodi*-p-*tolyldisulphoxide*, $S_2O_2(C_6H_3Me\cdot NO_2)_2$, pale yellow needles, m. p. 158°, is obtained together with the disulphide and the preceding sulphinic acid by the action of the calculated amount of 2*N*-sodium hydroxide on 3-nitro-4 chlorothioltoluene at 70—80°; it is also formed, in smaller amount but much more conveniently, by a curious reaction, viz., the action of chlorine on 3-nitro-*p*-tolyl methyl sulphide in commercial chloroform (following abstract). 3-*Nitro*-p-*toluenesulphinic acid*, $NO_2\cdot C_6H_3Me\cdot SO_2H$, almost colourless leaflets, has m. p. 116°.

3-*Nitro*-4-*aminothioltoluene*, $NO_2\cdot C_6H_3Me\cdot S\cdot NH_2$, orange-yellow needles, m. p. 147°, obtained by the action of ammonia on the chlorothiol in dry ether, reacts with acetic anhydride, benzaldehyde, and acetone respectively to form the *acetyl* derivative, yellow prisms,

m. p. 188° (decomp.), the *benzylidene* derivative, yellow needles, m. p. 146°, and the *compound*, $NO_2 \cdot C_6H_3Me \cdot S \cdot N:CMe_2$, yellow needles, m. p. 116°. It does not form salts, is reconverted into the chlorothiol by concentrated hydrochloric acid, and reacts with dilute acids or with hot glacial acetic acid to form the *imine*, $NH(S \cdot C_6H_3Me \cdot NO_2)_2$, yellow needles, m. p. 241° (decomp.).

In a similar manner the chlorothiol is converted by methylamine and by dimethylamine into 3-*nitro*-4-*methylaminothioltoluene*,

$$NO_2 \cdot C_6H_3Me \cdot S \cdot NHMe,$$

dark yellow needles, m. p. 46° (*methylimine*, $C_{15}H_{15}O_4N_3S_2$, m. p. 226° [decomp.]), and 3-*nitro*-4-*dimethylaminothioltoluene*, yellow needles, m. p. 76°, respectively.

The chlorothiol also reacts with certain aromatic primary and secondary amines to form substances of the type $NO_2 \cdot C_6H_3Me \cdot S \cdot X$; the *anilide*, orange-yellow crystals, m. p. 91°, o-*toluidide*, brownish-red plates or leaflets, m. p. 140°; p-*toluidide*, yellowish-brown prisms, m. p. 81°, *methylanilide*, yellow crystals, m. p. 78°, α-*naphthalide*, orange-yellow needles, m. p. 143°, and β-*naphthalide*, small, orange-yellow needles, m. p. 177°, are described, all of which are decomposed into the original amine and the chlorothiol by concentrated hydrochloric acid. The chlorothiol also reacts with α- and with β-naphthylamines in boiling glacial acetic acid to form 2 : 4-*bis*-3′-*nitro*-p-*tolylthiol*-α-*naphthylamine*, $NH_2 \cdot C_{10}H_5(S \cdot C_6H_3Me \cdot NO_2)_2$, and 3-*nitro*-4(α-3′-*nitro*-p-*tolylthiol*-β-*naphthylaminothiol*)*toluene*,

$$NO_2 \cdot C_6H_3Me \cdot S \cdot C_{10}H_6 \cdot NH \cdot S \cdot C_6H_3Me \cdot NO_2,$$

yellowish-brown crusts, m. p. 184°, respectively. The former has been obtained in two modifications, golden leaflets, m. p. 137°, and olive-green needles, m. p. 174°, which are interconvertible, and forms an *acetyl* derivative, $C_{26}H_{21}O_5N_3S_2$, pale yellow needles, m. p. 210°, whilst the latter, by heating with glacial acetic and concentrated hydrochloric acids, is converted into 3-*nitro*-p-*tolyl* α-2-*aminonaphthyl sulphide*, $NO_2 \cdot C_6H_3Me \cdot S \cdot C_{10}H_6 \cdot NH_2$, orange-red needles or plates, m. p. 150° (*hydrochloride*, pale yellow needles; *acetyl* derivative, yellow plates, m. p. 136°).

3-Nitro-4-chlorothioltoluene reacts with dimethylaniline in boiling benzene to form p-*dimethylaminophenyl* 3-*nitro*-p-*tolyl sulphide*,

$$NMe_2 \cdot C_6H_4 \cdot S \cdot C_6H_3Me \cdot NO_2,$$

red needles or prisms, m. p. 176°, which forms a yellow *hydrochloride*.

3-Nitro-4-chlorothioltoluene reacts with phenols in chloroform or hot toluene to form sulphides, the sulphur atom becoming attached to the phenolic nucleus; p-*hydroxyphenyl* 3-*nitro*-p-*tolyl sulphide*,

$$OH \cdot C_6H_4 \cdot S \cdot C_6H_3Me \cdot NO_2,$$

dark yellow plates, m. p. 128° (*acetyl* derivative, sulphur-yellow crystals, m. p. 90°), 3-*nitro*-p-*tolyl* α-4-*hydroxynaphthyl sulphide*, brown crusts, m. p. 205° (*acetyl* derivative, citron-yellow needles, m. p. 149°), and 3-*nitro*-p-*tolyl* α-2-*hydroxynaphthyl sulphide*, citron-yellow needles, m. p. 129° (*acetyl* derivative, pale yellow crystals, m. p. 124°), have been prepared.

The chlorothiol reacts with boiling acetone and with acetophenone in boiling chloroform to form the *sulphides*,

$$NO_2 \cdot C_6H_3Me \cdot S \cdot CH_2 \cdot COMe,$$

intensely yellow leaflets, m. p. 117°, and $NO_2 \cdot C_6H_3Me \cdot S \cdot CH_2 \cdot COPh$, yellow needles, m. p. 128°, respectively. C. S.

3-Nitro-*p*-tolyl Mercaptan. TH. ZINCKE and H. RÖSE (*Annalen*, 1914, **406**, 127—137).—3-Nitro-*p*-tolyl mercaptan is oxidised too easily to be isolated; its methyl, ethyl, and benzyl ethers have been prepared and examined.

3-*Nitro-p-tolyl methyl sulphide*, $NO_2 \cdot C_6H_3Me \cdot SMe$, yellow crystals, m. p. 77°, is obtained by heating 3 : 3′-dinitrodi-*p*-tolyl disulphide with aqueous alcoholic alkaline sodium sulphide and treating the cooled, diluted solution with methyl sulphate. Its behaviour with chlorine is very different under different experimental conditions. By chlorination in commercial chloroform it yields 3-nitro-4-chlorothioltoluene and a small amount of 3 : 3′-dinitrodi-*p*-tolyldisulphoxide (preceding abstract). By chlorination in chloroform saturated with water or containing alcohol, it yields 3-nitro-*p*-toluenesulphonyl chloride and 6-*chloro*-3-*nitro*-p-*tolylmethylsulphoxide*, $NO_2 \cdot C_6H_2MeCl \cdot SOMe$, pale yellow needles, m. p. 145°. By chlorination in glacial acetic acid containing a little water, it yields 3-nitro-*p*-toluenesulphonyl chloride. By chlorination in dry carbon tetrachloride, it yields an additive *compound*, $NO_2 \cdot C_6H_3Me \cdot SMeCl_2$, unstable, yellow crystals, which is decomposed by water, forming 3-*nitro*-p-*tolylmethylsulphoxide*,

$$NO_2 \cdot C_6H_3Me \cdot SOMe,$$

yellow needles, m. p. 105°. The last-named compound, which is also obtained by the oxidation of 3-nitro-*p*-tolyl methyl sulphide and by treating the following perbromide with water, is converted into the preceding chloronitro-*p*-tolylmethylsulphoxide by chlorination in carbon tetrachloride and into the *perbromide*, $NO_2 \cdot C_6H_3Me \cdot SMeBr_2$, orange-red needles, by the action of hydrogen bromide in glacial acetic acid. The perbromide is also formed by the action of bromine on 3-nitro-*p*-tolyl methyl sulphide in carbon tetrachloride.

3-*Nitro*-p-*tolyl ethyl sulphide*, $C_9H_{11}O_2NS$, yellow needles, m. p. 52°, is prepared and, in general, behaves in the same manner as the methyl ether; 3-*nitro*-p-*tolylethylsulphoxide*, $NO_2 \cdot C_6H_3Me \cdot SOEt$, pale yellow prisms, has m. p. 72°.

3-*Nitro*-p-*toluenesulphonyl chloride*, colourless crystals, m. p. 98—99°, yields a *sulphonylamide*, colourless leaflets, m. p. 170°, and *sulphonylanilide*, colourless needles, m. p. 129°.

By the reduction of 3-nitro-*p*-tolyl methyl sulphide in alcoholic solution by tin and hydrochloric acid, 3-*amino*-p-*tolyl methyl sulphide*, $C_8H_{11}NS$, b. p. 130°/20 mm., is obtained. It forms a *hydrochloride*, colourless needles, and *acetyl* derivative, colourless needles, m. p. 114°, and is oxidised by perhydrol in cold glacial acetic acid to the *azoxy*-derivative of the corresponding sulphone, $(CH_3 \cdot SO_2 \cdot C_6H_3Me)_2N_2O$, brownish-yellow needles, m. p. 254°.

By treating its diazotised solution with potassium iodide at 40—50° in the usual manner, the amino-sulphide yields 3-*iodo*-p *tolyl methyl sulphide*, C_8H_9IS, b. p. 153—154°/17 mm., which forms a *perbromide*, orange-red needles, and is converted into an *iodonitrotolylmethyl-sulphoxide* by concentrated nitric acid. C. S

β-Naphthol Sulphide and *iso*-*β*-Naphthol Sulphide. I. O. Hinsberg (*J. pr. Chem.*, 1914, [ii], **90**, 345—353).—In addition to the arguments advanced by Henriques (A., 1895, i, 103) and Nolan and Smiles (T., 1913, **103**, 346) in favour of the structural identity of *β*-naphthol sulphide and *iso*-*β*-naphthol sulphide, it is now ascertained that the *iso*-sulphide on treatment with quinoline and acetic anhydride yields a diacetyl derivative, a method which in cases hitherto observed has led only to the formation of *O*-acetyl compounds, and, further, although phenylhydrazine reacts with the *iso*-sulphide, there is no phenylhydrazone formed as would be expected if a ketonic structure were assumed. With a view to throwing more light on the isomerism, a study of the behaviour of the sulphides towards oxidising agents has been commenced.

β-Naphtholsulphoxide, $SO(C_{10}H_6{\cdot}OH)_2$, was obtained by the oxidation of *β*-naphthol sulphide suspended in acetic acid with 30% hydrogen peroxide at 30° for three weeks, and formed colourless prisms, m. p. 162° (decomp.). It gave with sulphuric acid a green, and with alcoholic ferric chloride a violet colour. On warming with acetic anhydride, dehydronaphthol sulphide (see below) was formed, but if boiled, a further reaction occurred with production of acetoxynaphthathioxin (compare T., 1912, **101**, 716).

By boiling for a few minutes with 5—10% sodium hydroxide and then acidifying with hydrochloric acid, *β*-naphthol sulphide was converted into *β*-naphthol. A similar decomposition was brought about by boiling with hydrochloric acid in acetic acid solution, and the formation of intermediate products, $O{:}C_{10}H_6{\cdot}SCl{\cdot}C_{10}H_6{\cdot}OH$ and $O{:}C_{10}H_6{:}S(ONa){\cdot}C_{10}H_6{\cdot}ONa$, is postulated, which are then further hydrolysed into *β*-naphthol and sulphur dioxide.

β-Naphtholsulphone, $SO_2(C_{10}H_6{\cdot}OH)_2$, was produced when *β*-naphthol sulphide was warmed with 30% hydrogen peroxide on the water-bath. It crystallised from acetic acid in prisms, and decomposed at 225°. With sulphuric acid it gave a blue, and with ferric chloride a violet coloration. Unlike the sulphoxide it is an extremely stable substance, unattacked by acids, alkali hydroxides, or zinc and hydrochloric acid. It is oxidised by potassium ferricyanide to *dehydro-β-naphtholsulphone*, $C_{10}H_6<^{SO_2}_{O\cdot O}>C_{10}H_6$, yellow crystals, m. p. 244°, insoluble in alkali hydroxides, and unaltered by boiling with acids.

Dehydro-β-naphthol sulphide, obtained by Henriques by oxidation of *β*-naphthol sulphide with potassium ferricyanide in alkaline solution (*loc. cit.*), was also prepared by oxidation with dichromate in acid solution. When oxidised with hydrogen peroxide, it is converted mainly into *β*-naphtholsulphone,

$$C_{10}H_6<^{-S-}_{O\cdot O}>C_{10}H_6 + H_2O_2 = SO_2(C_{10}H_6{\cdot}OH)_2.$$

Preference is given to the peroxide formula for dehydro-*β*-naphthol sulphide over the alternative quinone formula, because of the analogous method of formation of this substance and dehydro-*β*-naphtholsulphone, and its ready conversion into *β*-naphtholsulphone by oxidation. G. F. M.

Action of Organo-magnesium Compounds on Selenium Haloids. W. Strecker and A. Willing (*Ber.*, 1915, **48**, 196—206). —In extension of the discovery that sulphur chloride and thionyl chloride react with organo-magnesium compounds to form disulphides and sulphoxides respectively (A., 1910, i, 532), the authors have applied the same reactions to selenium dichloride and selenyl chloride. The former behaves in the normal way towards magnesium phenyl bromide, yielding diphenyl diselenide and diphenyl selenide, but with magnesium benzyl chloride it forms dibenzyl selenodichloride, $Se(C_7H_7)_2Cl_2$. It is supposed that some of the selenium dichloride is changed into the tetrachloride during the reaction, for the same compound is formed if the latter chloride is used at the outset. The assumption that the halogen comes from the selenium compound rather than from the Grignard reagent is justified by the fact that selenium dibromide and magnesium benzyl chloride yield dibenzyl selenodibromide.

When dibenzyl selenodichloride is treated with sodium hydroxide, it is converted into dibenzyl diselenide and benzaldehyde, which may be explained by the reactions: (I) $2Se(C_7H_7)_2Cl_2 = Se_2(C_7H_7)_2 + 2C_7H_7Cl + Cl_2$. (II) $C_7H_7Cl + NaOH = C_7H_7{\cdot}OH + NaCl$. (III) $2NaOH + Cl_2 = NaClO + NaCl + H_2O$. (IV) $C_7H_7{\cdot}OH + NaOCl = C_6H_5{\cdot}CHO + NaCl + H_2O$.

Dibenzyl selenide is converted into the above dichloride by the action of chlorine, whereas bromine yields a dibromide and finally a tetrabromide (Fromm and Martin, A., 1913, i, 1323). The selenodibromide also yields dibenzyl diselenide when treated with alcoholic sodium hydroxide, but aqueous alkali transforms it into benzyl selenoxide (A., 1894, i, 88), which, again, is converted into the selenodichloride by hydrochloric acid.

Selenyl chloride, unlike thionyl chloride, gives rise to oxygen-free compounds; in the case of magnesium phenyl bromide, to diphenyl selenide, and with the benzyl chloride, to the above dibenzyl selenodichloride.

An ethereal solution of selenium dichloride was slowly added to magnesium phenyl bromide, and the product was decomposed by cold sulphuric acid and extracted with ether. On distilling the extract, diphenyl selenide, b. p. 159°/10 mm. (bromide, m. p. 141°), and diphenyl diselenide, m. p. 200—208°/10 mm., m. p. 62·5°, were isolated. The latter forms a *tetrabromide*, red needles, m. p. 111°, which is quantitatively re-converted into the diselenide by warm alkalis.

Magnesium benzyl chloride was similarly treated with selenium dichloride. The dried ethereal extract deposited *dibenzyl selenodichloride*, white needles, m. p. 128°, and the mother liquors contained dibenzyl diselenide, m. p. 90°. *Dibenzyl selenodibromide*, $Se(C_7H_7)_2Br_2$, was prepared either from selenium dibromide and magnesium benzyl bromide or by the addition of the required amount of bromine to a cold ethereal solution of the diselenide. It forms yellow needles, m. p. 105·5°, and is freely soluble in chloroform.

J. C. W.

Action of Phosphoric Acid on Di-α-naphthylcarbinol. A. E. TSCHITSCHIBABIN and O. J. MAGIDSON (*J. pr. Chem.*, 1914, [ii], **90**, 168—177).—The reduction of di-α-naphthylcarbinol in acetic acid solution with zinc and hydrochloric acid furnishes, in addition to the by-products, dinaphthafluorene and tetranaphthylethane, which alone were observed by Schmidlin and Massini (A., 1909, i, 561), a resinous residue after evaporation of the benzene extract of the reaction product. This, after distillation in a vacuum and crystallisation from alcohol, yielded the main product of the reduction, dinaphthylmethane, m. p. 109°. The formation of dinaphthafluorene is to be regarded as due to the abstraction of water from the carbinol by the zinc chloride, resulting in the intermediate formation of dinaphthylmethylene. With the object of isolating dinaphthylmethylene, if under ordinary conditions it is sufficiently stable, or, failing that, the products of its isomerisation or polymerisation, the action of other dehydrating agents on the carbinol was tried, and anhydrous phosphoric acid was found to give the best results.

Dinaphthylcarbinol warmed with glacial phosphoric acid at 155° was converted into dinaphthylcarbinyl ether, $O[CH(C_{10}H_7)_2]_2$, which formed colourless crystals, m. p. 246·5°. It gives with sulphuric acid the same bluish-green coloration as the carbinol.

When heated with glacial phosphoric acid, gradually increasing the temperature during three-quarters to one hour up to 175°, and then continuing the heating for another half hour, dinaphthylcarbinol loses per molecule a molecule of water. The reaction product no longer gives a coloration with sulphuric acid, and after removing the phosphoric acid by boiling with water and crystallising the residue from benzene, a 60% yield of *dinaphthafluorene* was obtained.

From the dinaphthafluorene mother liquors another hydrocarbon was isolated and purified by repeated crystallisation from benzene, toluene, and, finally, a mixture of chloroform and ether. It formed fine colourless crystals which softened at 280°, and melted to a greenish liquid at 322°. From analyses and molecular weight determinations it is provisionally assumed to be *tetranaphthylethylene*, $C(C_{10}H_7)_2{:}C(C_{10}H_7)_2$. It does not absorb bromine, nor is it appreciably attacked by alkaline permanganate.

The following derivatives of dinaphthafluorene are described: Dinaphthafluorenone, formed by oxidation of the hydrocarbon with chromic acid. Red crystals, m. p. 269—270°. Schmidlin and Huber gave 255°.

Di-α-naphthafluorenol, obtained by reduction of dinaphthafluorenone with zinc dust and ammonia in alcoholic solution. Colourless needles, m. p. 246·5°.

Dinaphthafluorenecarboxylic acid, formed by the action of carbon dioxide on magnesium halogen dinaphthafluorene obtained by the action of magnesium ethyl bromide on the hydrocarbon. When crystallised from acetic acid, it forms snow-white needles of the composition

$$CH(C_{10}H_6)_2{\cdot}CO_2H,CH_3{\cdot}CO_2H,$$

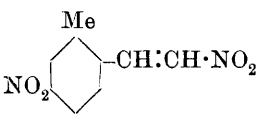
which lose the acetic acid at 100°. The pure acid crystallises from ether in tablets, m. p. 220—222°, with loss of carbon dioxide. The

salts are very unstable, and decompose spontaneously, especially when slightly warmed, into dinaphthafluorene and a carbonate. G. F. M.

Fungosterols. I. Substance of a "Sterol" Nature obtained from Lycoperdon gemmatum. T. Ikeguchi (*Zeitsch. physiol. Chem.*, 1914, **92**, 257—260).—The new *substance*, $(C_{10}H_{16}O)_n$, is obtained from the material extracted by ether from the dried fungus by washing with small quantities of ether and then recrystallising from alcohol. It crystallises in needles, m. p. 283—284°, $[\alpha]_D$ – 65·2°, insoluble in water, soluble in chloroform and benzene. It gives positive Liebermann, Liebermann-Burchard, Salkowski, and other "sterol" reactions. A crystalline bromine additive product could not be obtained, and the compound only slightly inhibited hæmolysis by saponin. H. W. B.

Diphenylaminoacetic Acid. R. Stollé (*J. pr. Chem.*, 1914, [ii], **90**, 273—275).—*Ethyl diphenylaminoacetate*, b. p. 205°/20 mm., was obtained by heating diphenylamine with diazoacetic ester in small portions in an air-bath at 120—130°, and fractionating the product under reduced pressure. The free *acid* was obtained by saponifying the ester with potassium hydroxide, or, directly, by heating monochloroacetic acid with diphenylamine at 180—200° for forty to fifty hours, either in an open vessel or in an autoclave in an atmosphere of carbon dioxide. It crystallised in needles, m. p. 113°. It decomposes at 110—120° with liberation of carbon dioxide, and with nitric acid gives an intense reddish-violet coloration, probably due to the intermediate formation of diphenylmethylamine. G. F. M.

Nitration of *o*-Methylcinnamic Acid. Hartwig Franzen and Walter Schneider (*J. pr. Chem.*, 1914, [ii], **90**, 547—551).—Attempts have been made to prepare 6-nitro-2-methylbenzaldehyde by nitrating *o*-methylcinnamic acid and oxidising the 6-nitro-2-methylcinnamic acid which should be formed. Fuming nitric acid acts readily on *o*-methylcinnamic acid, but the only products that could be separated, and these only in poor yields, were: (1) *β-4-dinitro-2-methylstyrene* (annexed formula), which forms dirty yellow needles, m. p. 163° (decomp.), and yields 4-nitrophthalic acid on oxidation by means of permanganate, and (2) *4-nitro-2-methylcinnamic acid*, $NO_2 \cdot C_6H_3Me \cdot CH:CH \cdot CO_2H$, which forms almost colourless needles, m. p. 256°, and yields 4-nitro-*o*-toluic and 4-nitrophthalic acids on oxidation with alkaline permanganate. T. H. P.



Salts of *o*-Acetoxybenzoic Acid. O. Gerngross and Hormaz Kersasp (*Annalen*, 1914, **406**, 240—260).—Detailed directions are given for the preparation of the following salts: *sodium*, m. p. 218° (decomp. corr.); *potassium*, m. p. 65° (corr.); *lithium*; *magnesium*; *calcium*; *zinc*; *copper*; *silver*, and *mercuric*. The last-mentioned salt crystallises from ethyl alcohol in prisms containing 1Et·OH, m. p. 82—84° (corr.) when rapidly heated, or about 136° (decomp. corr.), sintering at about 80°, when slowly heated; the air-dried salt has

m. p. 112° (decomp. corr.). By exposure to air, the alcohol is replaced by water, and the hydrated salt, needles containing $1H_2O$, is obtained; the anhydrous salt has m. p. 142° (decomp. corr.) when rapidly heated, but by prolonged heating at 100—105° forms a glassy mass, the substance now no longer containing ionisible mercury.

Compounds of mercuric *o*-acetoxybenzoate with mercuric chloride, $C_9H_7O_4ClHg$, plates, m. p. 154° (corr.), and with mercuric cyanide, $C_{10}H_7O_4NHg$, prisms, m. p. 183° (decomp. corr.), are described; also a double *compound* of mercuric benzoate and cyanide, $C_8H_5O_2NHg,H_2O$, large prisms, m. p. 107—109° (decomp. corr.).

The velocity of hydrolysis of the preceding sodium, potassium, calcium, and magnesium salts in aqueous solution at 60° has been investigated. The reaction appears to be of the first order (compare Rath, A., 1908, ii, 94), but the velocity constant shows a small, but very regular decrease owing to the retarding influence of the acetic acid liberated during the hydrolysis; this is proved by following the course of the hydrolysis in the presence of a large excess of sodium salicylate, of 1 mol. of acetic acid, and of 1 mol. of hydrochloric acid respectively.

C. S.

Dithiosalicylide. Richard Anschütz and Engelbert Rhodius (*Ber.*, 1914, **47**, 2733—2735).—By distillation of *o*-acetylthiolbenzoic acid under a pressure of 15—17 mm., it has been possible to obtain two new decomposition products in addition to diphenyl disulphide and thioxanthone already described as obtainable in this way. One of these compounds is *dithiosalicylide*, $C_6H_4<^{CO\cdot S}_{S\cdot CO}>C_6H_4$, prismatic crystals from acetic acid or rectangular leaflets from the dilute acid, m. p. near 175° with rapid heating; as when heated to 200—300° it is converted largely into thioxanthone, the formation of the latter is probably only a secondary change in the distillation of *o*-acetylthiolbenzoic acid. The other new decomposition product is designated *dibenzothiopten*, $C_6H_4<^{S\cdot C}_{C\cdot S}>C_6H_4$ or $C_6H_4<^{S\cdot C\cdot S}_{\quad C}>C_6H_4$; this forms lustrous, apparently rhombic leaflets, m. p. 216°, and gives a blue coloration with isatin and sulphuric acid.

D. F. T.

Number of Isomerides of Merotropic and Desmotropic Compounds. VI. Isomeric Modifications of Formylphenylacetic Ester. Arthur Michael (*Annalen*, 1914, **406**, 137—151. Compare A., 1912, i, 631, 861).—The author confirms Wislicenus's observation (A., 1912, i, 623) that the γ-ester under suitable conditions develops a transitory blue or bluish-violet coloration with alcoholic ferric chloride. In reply to his statements (*loc. cit.*) concerning the number and the nature of the modifications, experiments with various mixtures of the α- and the γ-esters are described, the results of which indicate that the presence of 5% of the liquid ester is manifested by the appearance of the mixture, its behaviour on heating, its m. p., and the reaction with ferric chloride; moreover, the α-ester can be removed by extracting the mixtures with light petroleum. The existence of a

special modification which can only occur in solution in alcohol is denied on various grounds. C. S

Optically Active *N*-Monomethyl Derivatives of Alanine, Leucine, Phenylalanine, and Tyrosine. EMIL FISCHER and WERNER LIPSCHITZ (*Ber.*, 1915, **48**, 360—378).—Monomethyl derivatives of α-amino-acids have been prepared by the action of methylamine on the corresponding bromo-acids, but only in the racemic form. Since the application of this method to the isolation of the corresponding, optically active forms is rendered difficult both on account of the difficulty of preparing the pure active bromo-acids and also of the danger of racemisation or Walden inversion during the action of the methylamine, the authors have applied the method of methylation of Fischer and Bergmann (A., 1913, i, 710) to optically active amino-acids and have obtained the *N*-monomethyl derivatives of *d*-alanine, *l*-leucine and of both the optically-active phenylalanines. In the case of tyrosine, the process is less satisfactory, since a *ditoluenesulphonyl* derivative is formed from which, after methylation, the two toluenesulphonyl groups can only be removed with difficulty. Tyrosine ethyl ether has therefore been converted into its *monotoluenesulphonyl* derivative, and the *acid* obtained from it, subjected to the action of an excess of methyl iodide, whereby the *compound*,

$$C_6H_4(OMe)\cdot CH_2\cdot CH(CO_2H)\cdot NMe\cdot SO_2\cdot C_7H_7,$$

is formed. This is converted by fuming hydriodic acid and phosphonium iodide into N-*methyltyrosine*. Starting from natural *l*-tyrosine, a dextrorotatory *N*-methyltyrosine is obtained, which, however, without doubt has the same configuration as the parent substance, and hence is termed *l*-*N*-methyltyrosine. The identity of this with natural rhatanin is confirmed (compare this vol., i, 138).

p-Toluenesulphonyl-*d*-alanine, m. p. 134—135° after softening at 130°, $[\alpha]_D^{20}$ −6·81° in alcoholic solution, is prepared by the action of *p*-toluenesulphonyl chloride dissolved in ether on a solution of *d*-alanine in aqueous sodium hydroxide. It forms well crystallised brucine and *quinine* salts; by the help of the latter the specific rotation can be raised to −7·26°, whereas Gibson (P., 1914, **30**, 32) gives $[\alpha]_D^{25}$ −7·6°. It is hydrolysed by concentrated hydrochloric acid at 100° without appreciable racemisation to *d*-alanine hydrochloride. On treatment with methyl iodide and sodium hydroxide, *p*-toluenesulphonyl-*d*-alanine is converted into p-*toluenesulphonyl*-d-N-*methylalanine*, $CH_3\cdot CH(NMe\cdot SO_2\cdot C_7H_7)\cdot CO_2H$, m. p. 121·5—122·5° after softening at about 117°, $[\alpha]_D^{20}$ −6·67° in alcoholic solution, which, however, is possibly partly racemised during the process. This is transformed by hydrochloric acid (D 1·19) at 100° into d-N-*methylalanine hydrochloride*, m. p. about 165·5—166° (corr.), after sintering at 158°, $[\alpha]_D^{20}$ +5·77° in water, from which the free *base* is obtained by means of lead oxide. It crystallises with $1H_2O$ in needles, and has $[\alpha]_D^{20}$ +5·59° in aqueous solution. The dried substance has m. p. about 300° (corr.) when rapidly heated, the process being accompanied by partial decomposition and sublimation. The *copper* salt, $C_8H_{16}O_4N_2Cu,2H_2O$, forms blue, rhombic plates.

p-*Toluenesulphonyl*-l-*leucine*, m. p. 124° after previous softening, $[\alpha]_D^{20}$ +4·50° in alcoholic solution, is converted in the usual manner into p-*toluenesulphonyl*-l-N-*methyl-leucine*,

$$CHMe_2\cdot CH_2\cdot CH(NMe\cdot SO_2\cdot C_7H_7)\cdot CO_2H,$$

colourless, six-sided plates, m. p. 91—92° after previous softening, $[\alpha]_D^{18}$ −21·12° in alcoholic solution (*ammonium* salt, $C_{14}H_{20}O_4NS\cdot NH_4$, needles, m. p. about 136°). Concentrated hydrochloric acid or fuming hydriodic acid converts the sulphonyl derivative into l-N-*methyl-leucine*, $[\alpha]_D^{21}$ +20·76° in aqueous solution, which, when carefully heated, sublimes in needles with slight decomposition. It is soluble in 22·45 parts of water at 25°, and yields a well-crystallised *nitrate* and a *hydrochloride*, needles, $[\alpha]_D^{19}$ +21·57° in aqueous solution. The *copper* salt, $C_{14}H_{28}O_4N_2Cu,H_2O$, forms four- or six-sided plates.

p-*Toluenesulphonyl*-d-*phenylalanine*,

$$CH_2Ph\cdot CH(NH\cdot SO_2\cdot C_7H_7)\cdot CO_2H,$$

fine needles, m. p. 164—165° (corr.) after slight previous softening, $[\alpha]_D^{19}$ +2·42° in acetone, faintly lævorotatory in chloroform, is prepared in almost quantitative yield in the usual manner. The *sodium* salt, $C_{16}H_{16}O_4NSNa,3\frac{1}{2}H_2O$, *potassium* and *ammonium* salts are described. Excess of methyl iodide and sodium hydroxide transform it into p-*toluenesulphonyl*-d-*phenylmethylalanine*, m. p. 92—93°, $[\alpha]_D^{20}$ +32·63°. Since partial racemisation appears to occur, the substance is best purified by means of the *sodium* salt, $C_{17}H_{18}O_4NSNa,2H_2O$. d-N-*Phenylmethylalanine* is prepared by the action of hydrochloric acid, or, better, of fuming hydriodic acid on the sulphonyl derivative. It forms colourless needles, $[\alpha]_D^{18}$ −48·22° in *N*/10-sodium hydroxide, $[\alpha]_D^{20}$ −17·7° in *N*-hydrochloric acid. The specimen obtained, however, is probably not quite pure. The corresponding *hydrochloride*, $C_{10}H_{13}O_2N,HCl$, forms rectangular plates which readily lose hydrogen chloride.

A similar series of derivatives has been prepared from *l*-phenylalanine. p-*Toluenesulphonyl*-l-*phenylalanine*, m. p. 164—165° (corr.), has $[\alpha]_D^{20}$ −2·12° when dissolved in acetone (*sodium* salt, $C_{16}H_{16}O_4NSNa,3\frac{1}{2}H_2O$).

p-*Toluenesulphonyl*-l-*phenylmethylalanine*, m. p. 92·5—94°, $[\alpha]_D^{20}$ −32·43° in acetone (*sodium* salt, $C_{17}H_{18}O_4NSNa,2H_2O$). l-N-*Phenylmethylalanine*, $[\alpha]_D$ +49·74° in *N*/10-sodium hydroxide solution.

N-p-*Toluenesulphonyl*-l-*tyrosine ethyl ester*,

$$OH\cdot C_6H_4\cdot CH_2\cdot CH(NH\cdot SO_2\cdot C_7H_7)\cdot CO_2Et,$$

needles, m. p. 114°, $[\alpha]_D^{17}$ +6·76° in alcohol, is obtained by the action of *p*-toluenesulphonyl chloride on *l*-tyrosine ethyl ester. Treatment with 5*N*-sodium hydroxide and acidification with hydrochloric acid transforms it into N-p-*toluenesulphonyl*-l-*tyrosine*, needles or prisms, m. p. 187—188° (corr.), after slight previous sintering, $[\alpha]_D^{21}$ −0·85° in alcohol, $[\alpha]_D^{20}$ −8·58° in *N*/2-sodium hydroxide. It is converted by sodium hydroxide and methyl iodide into N-p-*toluenesulphonyl* O : N-*dimethyltyrosine*, $OMe\cdot C_6H_4\cdot CH_2\cdot CH(CO_2H)\cdot NMe\cdot SO_2\cdot C_7H_7$, four-sided plates, m. p. 141—142° after previous sintering, $[\alpha]_D^{20}$ −26·75° in alcohol, which is purified through the *sodium* salt. When this substance is treated with hydriodic acid (D 1·96) and phosphonium iodide, it is converted into *p*-tolyl mercaptan, m. p. 44—44·5° after softening at

43°, and *l*-*N*-methyltyrosine, $[\alpha]_D^{19}$ +19·79° in 10% hydrochloric acid solution. H. W.

Diacylamides. Otto Mumm, Hugo Hesse, and Hans Volquartz (*Ber.*, 1915, **48**, 379—391).—Although both structurally possible isomerides of dialkylamides, $R{\cdot}CO{\cdot}NHR_1$ and $R{\cdot}C(:NH){\cdot}OR_1$, are frequently known, the diacyl derivatives have, almost without exception, only been obtained in one form to which the constitution $R{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}R_1$ is ascribed. The authors have, therefore, attempted to isolate *O*-acylamides by shaking solutions of the acid imide chloride in ether or light petroleum with an aqueous solution of the sodium salt of that acid, the radicle of which it is desired to introduce into the molecule. The diacylamide is found in the ethereal solution or is precipitated. The reaction follows the course:

$$R{\cdot}CCl:NR_1 \xrightarrow{NaOAc} R{\cdot}C(OAc):NR_1;$$

the latter substance may then isomerise to $R{\cdot}CO{\cdot}NR_1Ac$.

That such isomeric change actually can occur is shown by the fact that benzanilideimide chloride and sodium *m*-nitrobenzoate yield the same substance as *m*-nitrobenzanilideimide chloride and sodium benzoate. The constitution of the product cannot be directly deduced, so that such substances are termed diacylamides throughout the paper.

The wandering of the acyl group might conceivably be checked by the use of a radicle of high molecular weight, or by steric hindrance due to the presence of a substituent in the *ortho*-position. Direct experiment in this direction did not lead to the desired results, since, on the one hand, the same product was obtained from benzanilideimide chloride and sodium triphenylacetate and from triphenylacetanilideimide chloride and sodium benzoate, whilst, on the other hand, the substance obtained from benzanilideimide chloride and sodium *o*-toluate [?] was identical with that obtained from *o*-nitrobenzanilideimide chloride [?] and sodium benzoate.

Employment of acids with widely varying dissociation constants led to rather more favourable results. Benzanilideimide chloride and sodium phenoxide gave, as primary product, the *O*-phenyl ester of benzanilide, $Ph{\cdot}C(:NPh){\cdot}OPh$, which is converted by heating into the isomeric benzo-diphenylamide, $Ph_2N{\cdot}C(:O){\cdot}Ph$.

Substances identical with those described above were obtained by the action of benzanilideimide chlorde on carboxylic acids in anhydrous ether or in pyridine.

Attempts have also been made to determine the constitution of the diacylamides by choosing the acid radicle in such a manner that opportunity is afforded for intramolecular ring closure. The constitution of the cyclic derivatives is then a guide to that of the amide. Thus sodium anthranilate and benzanilideimide chloride yield diphenylquinazolone (compare Mumm and Hesse, A., 1910, i, 771), and hence the the *o*-aminobenzoyl group must be attached to the nitrogen atom. On the other hand, the three isomeric nitrobenzanilideimide chlorides yield benzoylanthranil when treated with sodium anthranilate, and hence the aminobenzoyl group must be attached to oxygen:

$$NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}CPh:N{\cdot}C_6H_4{\cdot}NO_2 \xrightarrow{-C_6H_4(NO_2){\cdot}NH_2} C_6H_4\begin{<}N{=}CPh\\CO{\cdot}O\end{>}$$

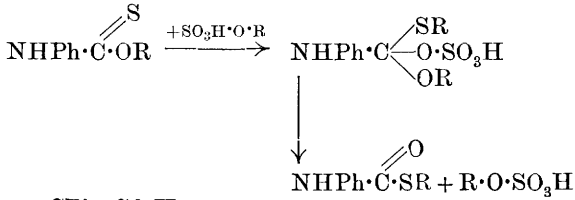
In certain cases, the constitution of the diacylamides can be directly deduced from the products of their decomposition. Thus dibenzoyloxanilide yields carbon monoxide and dioxide and benzoyldiphenylbenzamidine when heated above its m. p., and so must have at least one acyl group attached to oxygen.

The possibility is also discussed that the diacylamides represent equilibrium mixtures of *O*- and *N*-acyl derivatives; this would explain the frequent formation of *iso*nitriles from diacylamides which can scarcely be interpreted if both acyl groups are attached to the nitrogen atom. The following compounds are described, which, except when otherwise stated, are obtained by the method described above:

m-Nitrobenzoylbenzanilide, m. p. 142°. *Triphenylacetylbenzanilide*, needles, m. p. 185—186°. (*Triphenylacetanilide*, m. p. 167—168°; *triphenylacetanilideimide chloride*, prismatic rods, m. p. 137°). *Malonylmonobenzanilide*, $C_{16}H_{13}O_4N$, white prisms, m. p. 100—101° (decomp.); *succinylbenzanilide*, white prisms, m. p. 146—147°; *fumaryldibenzanilide*, m. p. 194° (decomp.); o-*toluoylbenzanilide*, m. p. 134—135°; *dibenzoyl*-o-*toluidide*, white prisms, m. p. 111—112°; *dibenzoyl*-o-*nitranilide*, four-sided plates, m. p. 182°; *dibenzoyl*-m-*toluidide*, white needles, m. p. 140—141°; *dibenzoyl*-p-*toluidide*, white prisms, m. p. 142—144°; *dibenzoyl*-m-*nitranilide*, white prisms, m. p. 150—151°; *dibenzoylmethylamide*, white, prismatic rods, m. p. 94—95°; *dibenzoylbenzylamide*, white prisms, m. p. 108°; *cinnamoylbenzoylbenzylamide*, white prisms, m. p. 113°; *O*-phenyl ether of benzanilide, m. p. 105°, which passes, when heated at 240°, into benzodiphenylamide, m. p. 180°; o-*nitrophenyl ether* of *benzanilide*, cubes, m. p. 116°; *benzopicrylanilide*, long needles, m. p. 195—196°, in which the trinitrophenyl radicle appears to be attached to nitrogen; *benzopicryl*-o-*toluidide*, pale yellow rhombs, m. p. 223—224°; o-*hydroxybenzoylbenzanilide*, white prisms, m. p. 189°; o-*hydroxybenzoylbenz*-o-*toluidide*, white needles, m. p. 122—123°; benzoylanthranil from the three isomeric benzonitranilideimide chlorides and sodium anthranilate; o-*methylaminobenzoylbenzanilide*, prisms, m. p. 188°, which by prolonged boiling with dilute hydrochloric acid is converted into an isomeric (probably cyclic) *substance*, m. p. 142°; *oxalyldibenzanilide*, white prisms, m. p. 212—213° (decomp.), which is converted at 220—230° into benzoyldiphenylbenzamidine, m. p. 172°; *oxalyldibenz*-o-*toluidide*, m. p. 171—173°; *dioxalyl*-p-*nitrobenzanilide*, white needles, m. p. 270° (decomp.), converted by boiling hydrochloric acid into 4-nitrophenyloxamic acid, m. p. 216°; benzanilide, from benzanilideimide chloride and potassium hydrogen oxalate, carbon monoxide and dioxide being evolved. H. W.

α-Thioldiphenylacetic Acid [Thiobenzilic Acid]. H. Becker and A. Bistrzycki (*Ber.*, 1914, **47**, 3149—3155).—The condensation of benzilic acid with phenylthiocarbimide has been studied. It was expected that either ring condensation would take place or that the acid would react like a simple alcohol. The product, however, was not an *O*-ester, but a compound in which the benzilic acid residue was attached to the sulphur atom, for it yielded thiobenzilic acid, aniline and carbon dioxide when warmed with dilute potassium hydroxide.

It is believed that an *O*-ester is first formed and an alkylsulphuric acid derivative of benzilic acid as a by-product. These combine and then the latter acid is eliminated from the compound in another direction, thus,



where R = $-CPh_2\cdot CO_2H$.

Benzilic acid was intimately mixed with phenylthiocarbimide and glacial acetic acid and gradually treated with concentrated sulphuric acid at 0°. The condensation product, *N-phenyl-S-benzhydrylthiocarbamate-α-carboxylic acid*, $NHPh\cdot CO\cdot S\cdot CPh_2\cdot CO_2H$, was precipitated by ice water. It forms colourless, microscopic prisms, decomp. 140·5°, which dissolve on rubbing with very dilute sodium carbonate solution, to be recovered if the solution is immediately acidified. On keeping, the alkaline solution deposits *s*-diphenylcarbamide, whereas on boiling the acid with 1% potassium hydroxide, it is hydrolysed to *α-thiol-diphenylacetic acid* [*thiobenzilic acid*], $SH\cdot CPh_2\cdot CO_2H$, colourless, microscopic tablets, m. p. 147·5—149°. Like benzilic acid, the latter yields a half-molecular proportion of carbon monoxide when warmed with concentrated sulphuric acid, and like thioglycollic acid it develops a violet colour when treated with very dilute ferric chloride and ammonia. It is converted by methyl sulphate and alkali into *methyl α-methylthioldiphenylacetate* [*methyl α-methylthiobenzilate*],

$$CH_3\cdot S\cdot CPh_2\cdot CO_2Me,$$

m. p. 66·5—67·5°, and is oxidised by ferric chloride to *dibenzhydryldisulpho-αα-dicarboxylic acid*, $S_2(CPh_2\cdot CO_2H)_2$, decomp. 174°, the *methyl* ester of which forms colourless prisms, m. p. 130·5—131·5°.

J. C. W.

αβ- and βα-Aminonaphthoic Acids. P. Friedländer and S. Littner (*Ber.*, 1915, **48**, 328—333).—α-Nitro-β-naphthylamine is prepared by the action of nitric acid (D 1·4) on a solution of acetyl-β-naphthylamine in glacial acetic acid and hydrolysis of the product with the calculated quantity of alcoholic potassium hydroxide. It is converted by diazotisation and treatment with potassium cuprocyanide into *α-nitro-β-naphthonitrile*, needles, m. p. 138°. Saponification with alkaline reagents causes the elimination of the nitro-group and formation of α-hydroxy-β-naphthoic acid, m. p. 185°. Reduction with iron filings and acetic acid transforms the nitro-nitrile into *α-amino-β-naphthonitrile*, colourless needles, m. p. 191—192°, which has only feeble basic properties. The amino-nitrile is very stable towards alkalis, but is converted by a solution of sodium in alcohol into *α-amino-β-naphthoic acid*, needles, m. p. 205° when rapidly heated, carbon dioxide being then evolved and α-naphthylamine formed. The basic properties are not very marked; concentrated hydrochloric acid

converts it into a sparingly soluble hydrochloride which is dissociated by water; on boiling the solution, carbon dioxide is evolved. The *ammonium* salt, needles readily soluble in water, the greyish-green *copper* salt, the white, crystalline *silver* salt, and the *sodium* salt are described.

The preparation of *β-amino-α-naphthoic acid*, colourless needles, m. p. 126° with loss of carbon dioxide, is conveniently effected by oxidation of naphthisatin in alkaline solution by means of lead peroxide. When dissolved in dilute hydrochloric acid, it slowly loses carbon dioxide in the cold, rapidly on warming. The *ammonium* and *alkali* salts are readily soluble; the *copper* salt $(C_{11}H_8O_2N)_2Cu$, forms a greyish-green, amorphous precipitate. The corresponding *acetyl* derivative, $C_{10}H_6{\cdot}NHAc{\cdot}CO_2H$, needles, m. p. 195—196°, retains the carboxyl group more firmly than the parent substance. H. W.

Alkylation of Ketones. A. Kötz and E. Lemien (*J. pr. Chem.*, 1914, [ii], **90**, 382—392)—The authors have made experiments to determine the extent to which alkyl radicles may be introduced into β-ketoneoxalic esters of the aliphatic and hydroaromatic series, and to ascertain the position taken up by the carbonylcarbethoxy-group,

$$\cdot CO{\cdot}CO_2Et,$$

in the interaction of ethyl oxalate and a mixed aliphatic ketone (compare Kötz and Blendermann, A., 1913, i, 1069).

From ethyl sodioacetoneoxalate [sodioacetylpyruvate], methyl, ethyl and benzyl derivatives of acetone may be obtained, but not the propyl or *iso*propyl derivatives, whereas from ethyl sodioacetonecarboxylate all these ketones are obtainable. As intermediate products, methyl- and ethyl-acetylpyruvic esters can be isolated, but not allyl- or benzyl-acetylpyruvic ester. For the velocity of introduction of the alkyls the order is the same for acetylpyruvic and acetonecarboxylic esters, namely, methyl, ethyl, allyl, benzyl, *iso*propyl and propyl, but in general the velocities are smaller in the latter case. Into ethyl 1-methyl-3-*cyclo*hexanone-4-pyruvate, the allyl radicle may be introduced, but not propyl or *iso*propyl (compare Augspurger, *Diss.*, Göttingen, 1913, and Wallach, "Terpene und Campher," 448). A second alkyl group cannot be introduced into the acetylpyruvic ester molecule.

That ethyl propionylpyruvate is formed when methyl ethyl ketone (1 mol.) and ethyl oxalate (1 mol.) interact in presence of sodium ethoxide is shown by the fact that, whilst ethyl acetylmethylpyruvate cannot be converted into ethyl acetyldimethylpyruvate, the isomeric ethyl propionylpyruvate should, from the above regularities in alkylation, be capable of methylation. When sodium ethoxide and methyl iodide act on ethyl propionylpyruvate, the latter is converted into 1 : 3-dimethyl*cyclo*pentane-2 : 4 : 5-trione, and that the conversion takes place by way of ethyl propionylmethylpyruvate and not *vid* 1-methyl*cyclo*pentane-2 : 4 : 5-trione follows from the fact that such methylpentanetrione cannot be methylated. Further, in presence of piperidine, ethyl propionylpyruvate reacts with benzaldehyde, giving ketopropionylphenylparacone, completely analogous to the ketoacetyl-phenylparacone obtained by Ruhemann from ethyl acetylpyruvate and benzaldehyde (T., 1906, **89**, 1236); if, on the other hand, methyl

ethyl ketone and ethyl oxalate yielded ethyl acetylmethylpyruvate, ethyl β-phenyl-β-hydroxypropionylmethylpyruvate,

$$CO_2Et\cdot CO\cdot CHMe\cdot CO\cdot CH_2\cdot CHPh\cdot OH,$$

and thence the pyrone derivative, $CH_2<\begin{matrix}CHPh\cdot O\\ CO-CMe\end{matrix}>C\cdot CO_2Et$, should be formed.

Ethyl acetylmethylpyruvate, $CHMeAc\cdot CO\cdot CO_2Et$, obtained from ethyl sodioacetylpyruvate by the action of methyl iodide or sulphate, is a yellow oil, b. p. 221°.

Ethyl acetylethylpyruvate, $CHEtAc\cdot CO\cdot CO_2Et$, formed by treating ethyl sodioacetylpyruvate with ethyl iodide or *p*-toluenesulphonate, is a dark yellow oil, b. p. 235°.

Ethyl acetylallylpyruvate, $CH_2{:}CH\cdot CH_2\cdot CHAc\cdot CO\cdot CO_2Et$, cannot be distilled, even in a vacuum, without decomposition, and is converted into allylacetone by alcoholic potassium hydroxide. Similar behaviour is shown by ethyl acetylbenzylpyruvate.

1 : 3-*Dimethylcyclopentane*-2 : 4 : 5-*trione*, $CHMe<\begin{matrix}CO\cdot CO\\ CO\cdot CHMe\end{matrix}$, forms long needles, m. p. 142°, with previous softening. When carefully heated for a long time above its melting point, it is converted into the *lactone*, $CHMe{:}C<\begin{matrix}CHMe\cdot CO\\ O-----CO\end{matrix}$, m. p. about 68°, which is reduced by hydrogen in presence of palladium chloride to the *compound*,

$$CHEt<\begin{matrix}CHMe\cdot CO\\ O-----CO\end{matrix}.$$

When distilled or when heated with the corresponding proportion of sodium ethoxide, ethyl propionylpyruvate yields 1-methyl*cyclo*pentane-2 : 3 : 5-trione.

Ketopropionylphenylparacone, $COEt\cdot CH<\begin{matrix}CO-----CO\\ CHPh\cdot O\end{matrix}$, forms white needles, m. p. 177—178°, exhibits acidic properties, and gives a deep red coloration with alcohol and ferric chloride. T. H. P.

Transformation of *o*-Cyanobenzoylated Diacylmethanes. JOHANNES SCHEIBER and FRIEDRICH HANN (*Ber.*, 1914, **47**, 3326—3335).—*o*-Cyanobenzoylated products are to be expected from the action of *o*-cyanobenzoyl chloride on the sodium derivatives of diacylmethanes. Such products are frequently unstable, passing, by loss of an acyl group, into β-acylated iminoketohydrindenes:

$$CN\cdot C_6H_4\cdot CO\cdot CH(ac)_2 \longrightarrow [CN\cdot C_6H_4\cdot CO\cdot CH_2ac] \longrightarrow C_6H_4<\begin{matrix}C{:}NH\\ -CO-\end{matrix}>CHac.$$

This process has been observed with all diacylmethanes which contain the acetyl group, the latter being eliminated. *o*-Cyanobenzoylacetonylacetone could not be obtained, ethyl *o*-cyanbenzoylacetoacetate only under certain conditions, whilst *o*-cyanobenzoyl-benzoylacetone is not completely stable. On the other hand, the transformation was not observed with ethyl *o*-cyanobenzoylcyanoacetate, whilst indefinite results were obtained with the malonic ester derivative.

Ethyl o-cyanobenzoylacetoacetate, $CN\cdot C_6H_4\cdot CO\cdot CHAc\cdot CO_2Et$, *ethyl-*

3-*iminohydrindone*-2-*carboxylic ester*, $C_6H_4<\begin{matrix}C(NH)\\CO\end{matrix}>CH\cdot CO_2Et$, and *ethyl iminophthalylacetoacetate*, $C_6H_4<\begin{matrix}C(NH)\\CO\end{matrix}>CAc\cdot CO_2Et$ (?); are formed by the action of *o*-cyanobenzoyl chloride or ethyl sodioacetoacetate in the presence of benzene, the first and second being produced in cold, the second and third in warm solution. The first-named substance forms needles which melt at 65° and decompose at 190°. It can be preserved in a desiccator, but on exposure to air, gradually passes into the second compound. The latter consists of shining, lemon-yellow needles, m. p. 242°, and yields a mixture of substances when treated with phenylhydrazine. Sodium hydroxide or concentrated hydrochloric acid causes the replacement of the imino-group by oxygen with formation of diketohydrindene, m. p. 130°, and anhydrobisdiketohydrindene, m. p. 206°, respectively; reduction with zinc dust and glacial acetic acid gives *ethyl hydrindone*-2-*carboxylate*, m. p. 144—145°. Ethyl iminophthalylacetoacetate forms yellow needles, m. p. 129°.

o-Cyanobenzoyl chloride and ethyl sodiomalonate yield only products which, after removal of excess of malonic ester under 4—5 mm. pressure, gradually deposit phthalimide.

Ethyl o-*cyanobenzoylcyanoacetate*, $CN\cdot C_6H_4\cdot CO\cdot CH(CN)\cdot CO_2Et$, m. p. 115—116°, is prepared by the action of *o*-cyanobenzoyl chloride (1 mol.) on ethyl sodiocyanoacetate (2 mols.). It can be preserved unchanged, and yields a *phenylhydrazone*, yellowish-brown crystals, m. p. 198°. When the reagents are used in equimolecular proportions, o-*cyanobenzoic anhydride*, shining leaflets, m. p. 181—182°, is also formed.

Di-o-*cyanobenzoylacetylacetone*, $CAc_2(CO\cdot C_6H_4\cdot CN)_2$, white crystals, m. p. 139—140°, and 3-*imino*-2-*acetylhydrindone*, yellow leaflets, m. p. 247—248°, are obtained by the interaction of *o*-cyanobenzoyl chloride and sodioacetylacetone in benzene or ether. The former loses an *o*-cyanobenzoyl and an acetyl group under the influence of sodium alkyloxide and gives o-*cyanobenzoylacetone*, needles, m. p. 85°. Sodium hydroxide converts the latter into diketoacetylhydrindene, m. p. 110°.

o-Cyanobenzoyl chloride reacts incompletely with the sodium derivative of benzoylacetone in ether or benzene. The main product is *o*-cyanobenzoylbenzoylacetone, $CN\cdot C_6H_4\cdot CO\cdot CHAc\cdot COPh$, needles, m. p. 145°. 3-*Imino*-2-*benzoylhydrindone*, yellow crystals, m. p. 237°, is also produced in small quantity; when treated with sodium hydroxide it evolves ammonia and gives benzoyldiketohydrindene, m. p. 108°. H. W.

Replacement of the Halogens of Halogen Acid Imides by Organic Radicles. Johannes Scheiber and Friedrich Hann (*Ber.*, 1914, **47**, 3335—3344).—The authors have studied the condensation of bromophthalimide and bromosuccinimide with ethyl sodioacetoacetate and similar substances. Instead of the expected carbimides or their derivatives, products of the type $R<\begin{matrix}CO\\CO\end{matrix}>N\cdot CH(ac)_2$ or

$$CH(A)_2\cdot CH(A)_2$$

are obtained (A = CO_2Et, COMe, COPh, or CN); the carbethoxyl group favours the formation of substances of the latter type, whilst the acetyl and benzoyl radicles cause the production of compounds of the former class; the cyanogen group resembles the carbethoxyl, but inhibits both reactions to a considerable extent.

Bromophthalimide reacts with ethyl sodioacetoacetate in benzene, ether, or alcohol-ether with formation of ethyl diacetylsuccinate, m. p. 88—89°, phthalimide, and *ethyl α-phthaliminoacetoacetate*,

$$C_6H_4{:}(CO)_2{:}N{\cdot}CHAc{\cdot}CO_2Et,$$

white needles, m. p. 94°. The latter is converted by boiling concentrated hydrochloric acid into phthalic acid and ethyl α-aminoacetoacetate hydrochloride. With phenylhydrazine in glacial acetic acid solution, it yields 4-phthalimino-1-phenyl-3-methyl-5-pyrazolone,

$$C_6H_4{:}(CO)_2{:}N{\cdot}CH\begin{cases}CMe{:}N\\ CO—NPh\end{cases}',$$

pale yellow crystals, m. p. 270°, and small quantities of a *substance*, orange needles, m. p. >250°, which is probably the phenylhydrazide-phenylhydrazone,

$$NHPh{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CH(CO_2Et){\cdot}CMe{:}N{\cdot}NHPh.$$

Ethyl ethanetetracarboxylate, m. p. 77°, and phthalimide are produced by the interaction of bromophthalimide and ethyl sodiomalonate in ether or benzene. When, however, an alcoholic solution of the sodiomalonate is added to an ethereal suspension of bromophthalimide, ethyl phthaliminomalonate is formed in 20% yield, together with much phthalimide.

Ethyl phthaliminocyanoacetate could not be obtained from bromophthalimide and ethyl sodiocyanoacetate. In its place, ethyl dicyanosuccinate, m. p. 120—121°, is produced in small yield, together with phthalimide and a *substance*, $C_{12}H_{16}O_8N$, yellow needles, m. p. 73°, which is probably formed by the action of hypobromous acid on ethyl cyanoacetate.

Phthaliminoacetylacetone, $C_6H_4{:}(CO)_2{:}N{\cdot}CHAc{\cdot}COMe$, white, shining needles, m. p. 120—121°, is readily formed from bromophthalimide and sodioacetylacetone in benzene. It slowly dissolves in boiling concentrated hydrochloric acid, yielding phthalic acid and a substance which behaves in the manner to be expected of *aminoacetylacetone*, and which is still under investigation. With phenylhydrazine it yields the *pyrazole*, $C_6H_4{:}(CO)_2{:}N{\cdot}C\begin{cases}CMe{:}N\\ CMe{:}NPh\end{cases}$, needles, m. p. 144—145°.

Similar compounds are readily obtained from benzoylacetone. *Phthaliminobenzoylacetone* forms shining prisms, m. p. 116°, gives with concentrated hydrochloric acid, phthalic acid and *aminobenzoylacetone*, and with phenylhydrazine, the *pyrazole*,

$$C_{24}H_{17}O_2N_3,$$

m. p. 150—151°.

Bromosuccinimide and ethyl sodioacetoacetate yield chiefly ethyl diacetylsuccinate with small quantities of a *substance*, m. p. 137°, which is probably ethyl succiniminoacetoacetate. With ethyl sodiomalonate and bromosuccinimide, ethyl ethanetetracarboxylate and succinimide are obtained in almost theoretical amount. Ethyl

sodiocyanoacetate gives *ethyl succiniminocyanoacetate*,

$$C_2H_4{\cdot}(CO)_2{\cdot}N{\cdot}CH(CN){\cdot}CO_2Et,$$

white needles, m. p. 110°, in poor yield.

Succiniminoacetylacetone, white prisms, m. p. 151·5°, is readily obtained in the usual manner. The corresponding pyrazole could not be prepared. It yields, however, a *disemicarbazone*, m. p. 257—258°, and gives aminoacetylacetone hydrochloride when boiled with concentrated hydrochloric acid. *s*-Tetra-acetylethane, m. p. 192°, is occasionally formed as by-product in the preparation of succiniminoacetylacetone.

Succiniminobenzoylacetone is prepared in the same manner as the previous compound. It forms white crystals, m. p. 140°, which gradually give a coloration with ferric chloride. Boiling hydrochloric acid converts it with difficulty into aminobenzoylacetone hydrochloride. With phenylhydrazine in glacial acetic acid solution, it yields the *pyrazole*, $C_{20}H_{17}O_2N_3$, glassy crystals, m. p. 193°.

H. W.

The Condensation of γ-Ketonic Acids with Phthalic Anhydride. W. Borsche (*Ber.*, 1914, **47**, 2708—2722).—In extension of the earlier discovery that compounds of the type of phenylbenzylidene-Δ$^{\gamma}$-butenolactone can be obtained by condensation of γ-ketonic acids with aromatic aldehydes in the presence of acetic anhydride, it has now been found that under similar conditions the γ-ketonic acids will also condense with phthalic anhydride, forming double lactones of a type,

$$\begin{matrix} CR{:}CH \\ | \\ O{-}{-}CO \end{matrix}\!\!>\!C{:}C\!<\!\begin{matrix} C_6H_4 \\ | \\ O \end{matrix}\!\!>\!CO,$$

hitherto unknown.

[With G. Heimbürger.]—When sodium *β-p*-toluoylpropionate is warmed with phthalic and acetic anhydrides for eight to ten hours, a deposit of *α-phthalidene-γ-p-tolyl-Δ$^{\gamma}$-butenolactone*,

$$C_6H_4Me{\cdot}\begin{matrix} C{:}CH \\ | \\ O{-}CO \end{matrix}\!\!>\!C{:}C\!<\!\begin{matrix} C_6H_4 \\ | \\ O \end{matrix}\!\!>\!CO,$$

orange-yellow needles, m. p. 266°, is obtained. On treatment with an equimolecular proportion of sodium ethoxide in alcoholic solution, this substance is slowly converted into the *sodium* derivative of *ethyl α-o-carbethoxybenzoyl-β-p-toluoylpropionate*,

$$C_6H_4Me{\cdot}CO{\cdot}CH_2{\cdot}C(CO_2Et){:}C(ONa){\cdot}C_6H_4{\cdot}CO_2Et,$$

yellow needles, m. p. 250° (decomp.); the formation of this compound is more rapid if a bimolecular proportion of sodium ethoxide is applied, the production of this compound under the former conditions being probably due to the presence of a little sodium ethoxide arising from alcoholysis of the first formed but unisolated

$$C_6H_4Me{\cdot}\begin{matrix} C{:}CH \\ | \\ O{-}CO \end{matrix}\!\!>\!C{:}C(ONa){\cdot}C_6H_4{\cdot}CO_2Et.$$

The ester corresponding with the isolated sodium derivative is evidently unstable, for on the addition of acid, the solid obtained consists of *α-o-carbethoxybenzoyl-γ-p-tolyl-Δ$^{\gamma}$-butenolactone*,

$$C_6H_4Me{\cdot}\begin{matrix} C{:}CH \\ | \\ O{-}CO \end{matrix}\!\!>\!CH{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2Et,$$

yellow leaflets, m. p. 131—132°, and then again near 230° after

resolidifying at an intermediate temperature. When dissolved in organic media, this lactone tends to change into a more fusible *isomeride* of α-phthalidene-γ-*p*-tolyl-Δ$^{\gamma}$-butenolactone, m. p. 226—227°, the existence of which is attributed to geometric isomerism dependant on the ethylenic bond. In its chemical behaviour the substance accords completely with its isomeride, m. p. 266°.

α-*o*-Carbethoxy-γ-*p*-tolyl-Δ$^{\gamma}$-butenolactone on benzoylation in pyridine solution gives a *benzoyl* derivative, probably

$$C_6H_4Me\cdot\overset{O-CO}{\overset{|}{C}}:CH\rangle C:C(OBz)\cdot C_6H_4\cdot CO_2Et,$$

needles, m. p. 154—155°, which easily undergoes decomposition into ethyl benzoate and the above dilactone, m. p. 226—227°; when treated with sodium hydroxide solution the lactone is converted into the *sodium* salt of α-*o*-carboxybenzoyl-β-*p*-toluoylpropionic acid,

$$C_6H_4Me\cdot CO\cdot CH_2\cdot CH(CO_2Na)\cdot CO\cdot C_6H_4\cdot CO_2Na,$$

m. p. above 250° (decomp.), from which the action of dilute hydrochloric acid does not liberate the corresponding acid, but a *lactone*, probably α-o-*carboxybenzoyl*-γ-p-*tolyl*-Δ$^{\gamma}$-*butenolactone*,

$$C_6H_4Me\cdot\overset{O-CO}{\overset{|}{C}}:CH\rangle CH\cdot CO\cdot C_6H_4\cdot CO_2H,$$

orange-red needles, m. p. 177—178° and then above 220° after intermediate solidification.

α-o-*Carbomethoxybenzoyl*-γ-p-*tolyl*-Δ$^{\gamma}$-*butenolactone*, obtained in the general manner, forms deep yellow leaflets, m. p. 140°; its chemical behaviour is similar to that of its ethyl analogue.

Both the isomeric phthalidenebutenolactones described above (as also their described derivatives), when warmed with sulphuric acid in methyl- or ethyl-alcoholic solution, undergo conversion into esters of 2-o-*carboxyphenyl*-5-p-*tolylfuran*-3-*carboxylic acid*

$$\overset{C(C_6H_4Me)}{\overset{\|}{CH}}\rangle O;$$
$$\underset{C(CO_2H):C(C_6H_4\cdot CO_2H)}{}$$

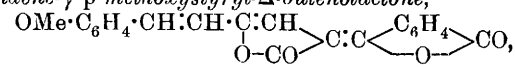
the *dimethyl* ester, prismatic crystals, m. p. 103°, and the *diethyl* ester, needles, m. p. 76—77°, were hydrolysed by aqueous-alcoholic sodium hydroxide to the free acid, glistening yellow crystals, m. p. 265—266° (decomp.), with a bluish-green fluorescence.

Condensation of β-benzoylpropionic acid with phthalic anhydride under the above conditions gives rise to α-*phthalidene*-γ-*phenyl*-Δ$^{\gamma}$-*butenolactone*, deep yellow needles, m. p. 263—264°, or yellowish-red leaflets, m. p. 228—229°, the two forms being the analogues of the two isomerides in the case of the corresponding phthalidene-*p*-tolyl-Δ$^{\gamma}$-butenolactone. Treatment with an equimolecular quantity of sodium ethoxide, followed by the addition of acid, converts the lactone into α-o-*carbethoxybenzoyl*-γ-*phenyl*-Δ$^{\gamma}$-*butenolactone*, yellow needles, m. p. near 78°. When heated with sulphuric acid in methyl-alcoholic solution, phthalidenephenylbutenolactone gives rise to the oily *methyl* ester of 2-o-*carboxyphenyl*-5-*phenylfuran*-3-*carboxylic acid*, from which by hydrolysis the free acid can be obtained in yellow needles, m. p. 263°, with a bluish-green fluorescence.

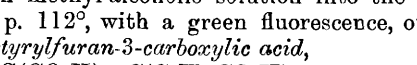
Lævulic acid resembles the γ-ketonic acids with aromatic substituents in readily condensing with phthalic anhydride, with formation of

α-phthalidene-γ-methyl-Δ$^{\gamma}$-butenolactone, yellow needles, m. p. 225—226°, but this substance, on treatment with sodium ethoxide, gave rise only to resinous products. The action of methyl-alcoholic sulphuric acid on the lactone yielded the oily *methyl* ester of 2-*o*-*carboxyphenyl*-5-*methylfuran*-3-*carboxylic acid*, which latter by hydrolysis was obtainable in yellow leaflets, m. p. 238—240°.

α-Phthalidene-γ-p-*methoxystyryl*-Δ-*butenolactone*,



deep red leaflets, m. p. 255°, obtained from sodium δ-anisylidenelevulate and phthalic anhydride in the general manner, was converted by sulphuric acid in methyl-alcoholic solution into the *methyl* ester, yellow needles, m. p. 112°, with a green fluorescence, of 2-*o*-*carboxyphenyl*-5-p-*methoxystyrylfuran*-3-*carboxylic acid*,



the free acid, yellow needles with a green fluorescence, m. p. 268—269°, being obtained by hydrolysis. D. F. T.

The Addition of Diacylmethanes to Compounds of the Type of Ethyl *iso*Propylidenemalonate. JOHANNES SCHEIBER and FRITZ MEISEL (*Ber.*, 1915, **48**, 238—266).—Whereas many compounds of the type R·CH:C·CO have been condensed with diacylmethanes, few of the type RR′C:C·CO have been examined, owing, of course, to the difficulty of obtaining the desired substances. Such compounds are mesityl oxide, ethyl dimethylacrylate and the condensation products of acetone with malonic, acetoacetic and cyanoacetic esters. Up to the present time, the only condensations with diacylmethanes which had been effected were normal in their course. They include the combination of mesityl oxide with acetoacetic and malonic esters, ethyl dimethylacrylate with malonic and cyanoacetic esters, *iso*propylideneacetoacetic ester with ethyl acetoacetate, and *iso*propylidenemalonic ester with ethyl malonate. Many other combinations have now been studied, partly with the expected results and partly with surprising complications.

A. *Experiments with ethyl* iso*propylidenemalonate.*—This ester was prepared in 39% yield by boiling ethyl malonate, acetone and acetic anhydride with zinc chloride, other condensing agents having no effect. It is only slowly attacked by ozone in carbon tetrachloride at −15°, the products being quite normal, namely, acetone and, apparently, ethyl mesoxalate, and it is converted into malondianilide only after prolonged heating with aniline.

A mixture of this ester (1 mol.) with ethyl sodioacetoacetate (2 mol.) in alcohol was heated under nearly 2 atmos. pressure for twenty hours, then diluted with water and extracted with ether ("alkaline" extract), and finally acidified and extracted again ("acid" extract). The first extract contained a little unchanged ester, whereas the acid extract contained a viscous oil which lost alcohol at about 180° and changed into a pale yellow, refractive, elastic substance, b. p. 190—195°. Both compounds gave dimethylhydroresorcinol on boiling with barium

hydroxide, the first of them is most probably *ethyl α-acetyl-ββ-dimethylpropane-αγγ-tricarboxylate* (I) and the other *ethyl* 3 : 5-*diketo*-1 : 1-*dimethyl*cyclo*hexane*-2 : 6-*dicarboxylate* (II).

(I) $CMe_2<^{CH(CO_2Et)_2}_{CHAc\cdot CO_2Et}$ → (II) $CMe_2<^{CH(CO_2Et)\cdot CO}_{CH(CO_2Et)\cdot CO}>CH_2$

It is remarkable that the former loses alcohol and not a carbethoxyl group on heating. Both esters react with phenylhydrazine, but only the former (I) with semicarbazide and hydroxylamine. The derivatives are those of the ester II in each case; *phenylhydrazone*, $C_{20}H_{26}O_5N_2$, pale yellow, m. p. 183—184°; *disemicarbazone*, $C_{16}H_{26}O_6N_6$, felted needles, m. p. 216°, soluble in alcohol, and *disemicarbazidesemicarbazone*, $C_{14}H_{24}O_6N_{12}$, m. p. 248°, insoluble in alcohol; and *bis*-iso*oxazolone*, $C_{10}H_{10}O_4N_2$, pale orange crystals, m. p. 195° (decomp.).

Ethyl *iso*propylidenemalonate yielded with α-methyl*iso*oxazole, that is, with sodiocyanoacetone (Claisen, A., 1892, 1072) under the same conditions, an acid extract which contained *ethyl γ-cyano-γ-acetyl-ββ-dimethylpropane-αα-dicarboxylate* (III.), which lost alcohol and formed *ethyl* 2-*cyano*-3 : 5-*diketo*-1 : 1-*dimethyl*cyclo*hexane*-6-*carboxylate* (IV), b. p. 190—200°/18 mm., on distillation.

(III.) $CMe_2<^{CHAc\cdot CN}_{CH(CO_2Et)_2}$ → (IV) $CO<^{CH_2\text{———}CO}_{CH(CN)\cdot CMe_2}>CH\cdot CO_2Et$

The original ester only reacted to a slight extent when heated for several days with alcoholic sodioacetylacetone and then formed an unexpected product, namely, *ethyl* 1 : 3-*dimethyl*-Δ^1-cyclo*butene*-4-*carboxylate*, $CH<^{CHMe}_{CMe}>CH\cdot CO_2Et$. This is a highly refractive, sweet smelling oil, b. p. 103—105°/18 mm., which has no ketonic properties, forms a monobromide, and yields the *acid*, $C_7H_{10}O_2$, m. p. 94°, on hydrolysis with barium hydroxide.

The reaction with ethyl sodiocyanoacetate followed an entirely different course and led to a product, m. p. 135° (see below, C), the formation of which entails the displacement of the malonic residue by the cyanoacetic residue. Benzylidenemalonic ester reacts normally with ethyl sodiocyanoacetate in the presence of sodium ethoxide, but suffers the same displacement in the presence of diethylamine, the product being ethyl α-cyanocinnamate, m. p. 51°.

B. *Experiments with ethyl* iso*propylideneacetoacetate*.—This ester (Pauly, A., 1897, i, 266) is also only slowly attacked by ozone, the products being acetone and ethyl diketobutyrate. It formed the same esters with ethyl sodiomalonate as above (I and II), but did not react with the sodium derivative of cyanoacetone or acetylacetone. With ethyl sodiocyanoacetate it yielded the product, m. p. 135° (C), and with methyl sodiocyanoacetate, the compound, m. p. 178° (D), the cyanoacetic residue again displacing the other ester group.

C. *Experiments with ethyl* iso*propylidenecyanoacetate*.—The condensation of acetone with ethyl cyanoacetate is influenced by the agent employed. Diethylamine gave an 8% yield (Komppa, A., 1901, i, 114), whereas methylamine hydrochloride gives a 25% yield, and aniline zinc chloride over 40%. The ester is, again, but slowly degraded by ozone, acetone and, apparently, the nitrile-ester of mesoxalic acid, $CN\cdot CO\cdot CO_2Et$, being formed. It is hydrolysed by

baryta to malonic acid, and it is not affected by hot aniline. With potassium ethoxide, it forms neither the normal acid nor dimethylacrylic acid, but the above *compound*, $C_{13}H_{14}O_2N_2$, m. p. 135°. This crystallises in glistening leaflets, dissolves in alkali carbonates, gives a green and then red coloration with ferric chloride, evolves hydrogen cyanide when kept, and reacts with phenylhydrazine and semicarbazide, although individual derivatives could not be isolated. For various reasons, the formula proposed is

$$CN\cdot CH\begin{matrix}CO\text{—}CH_2\\CHMe\cdot CH\end{matrix}\!\!>C\cdot CH(CN)\cdot CO_2Et.$$

The same substance is the sole product of the reaction between ethyl *iso*propylidenecyanoacetate and the sodium derivatives of ethyl malonate, acetoacetate or cyanoacetate.

D. *Experiments with methyl* iso*propylidenecyanoacetate.* This *ester*, $CMe_2{:}C(CN)\cdot CO_2Me$, was prepared by condensing acetone with methyl cyanoacetate in the presence of aniline zinc chloride. It is a highly refractive oil, b. p. 93—95°/7 mm., 104—105°/14 mm., m. p. 20—21°. With potassium methoxide it yielded the *methyl* homologue,

$$C_{12}H_{12}O_3N_2,$$

m. p. 178°, of the foregoing compound under C. This also gave no other characterisable derivatives than a mixture of two compounds with semicarbazide.

E. *Experiments with ethyl* iso*butylidenecyanoacetate.* This *ester* [*ethyl α-cyano-β-methyl-Δ$^{\alpha}$-pentenoate*] $C_9H_{13}O_2N$, was prepared from methyl ethyl ketone by the aniline-zinc chloride condensation. It has b. p. 104—108°, does not react with bromine or ferric chloride, but is hydrolysed in the normal way. With ethyl sodioacetoacetate, it yields the expected *ethyl 2-cyano-3 : 5-diketo-1-methyl-1-ethyl*cyclo*hexane-6-carboxylate*, $CO\begin{matrix}CH_2\text{————}CO\\CH(CN)\cdot CMeEt\end{matrix}\!\!>CH\cdot CO_2Et$, b. p. 165—175°/20 mm.

F. *Experiments with ethyl acetophenonylidenecyanoacetate.*—This *ester* [*ethyl α-cyano-β-methylcinnamate*], $C_{13}H_{13}O_2N$, was prepared in the same way. It has b. p. 157—158°/6 mm., is hydrolysed by barium hydroxide to malonic acid and acetophenone, and by cold, alcoholic potassium hydroxide to *α-cyano-β-methylcinnamic acid*, white needles, m. p. 173°. With ethyl sodioacetoacetate, it formed the normal product, *ethyl 2-cyano-3 : 5-diketo-1-phenyl-1-methyl*cyclo*hexane-6-carboxylate*, $CO\begin{matrix}CH_2\text{————}CO\\CH(CN)\cdot CMePh\end{matrix}\!\!>CH\cdot CO_2Et$, b. p. 210—220°/17 mm.

G. *Experiments with mesityl oxide.*—This compound only reacted to a slight extent with alcoholic sodioacetylacetone and yielded, in the acid extract, *3-keto-4-acetyl-1 : 5 : 5-trimethyl-Δ^1-*cyclo*hexene*,

$$CMe_2\begin{matrix}CH_2\text{–}CMe\\CHAc\cdot CO\end{matrix}\!\!>CH,$$

a terpene-like oil, b. p. 100—110°/18 mm., which reacted with semicarbazide to form the *semicarbazone*, $C_{12}H_{19}O_2N_3$, m. p. 167°, and the corresponding *pyrazole*, $C_{12}H_{17}ON_3$, m. p. 124°.

Mesityl oxide condensed with ethyl sodiocyanoacetate when heated in ether under a slight pressure. The alkaline extract contained an

oil which decomposed on distillation, b. p. above 200°/15 mm., into a very viscous product, the two substances being *ethyl α-cyano-γ-acetyl-ββ-dimethylbutyrate* (V) and *2-cyano-3 : 5-diketo-1 : 1-dimethyl*cyclo*hexane* (VI):

(V). $CMe_2<^{CH_2\cdot COMe}_{CH(CN)\cdot CO_2Et}$ → (VI). $CMe_2<^{CH_2\text{-----}CO}_{CH(CN)\cdot CO}>CH_2$.

The acid extract contained a solid which could not be distilled. This was the chief product when the condensation was carried out in the presence of excess of alkali ethoxide. It proved to be *ethyl α'-cyano-β'β'-dimethylacrylyl-α-cyanoacetate* [*αγ-dicyano-β-keto-δ-methyl-Δγ-hexenoate*] (VII), and it formed white prisms, m. p. 130°, dissolved in alkali carbonates, reacted with phenylhydrazine, yielded a *semicarbazone*, m. p. 204—205°, an *isooxazolone*, $C_9H_7O_2N_3$, m. p. 113°, and, with aniline, *α-cyano-β-anilino-β-methylbutyranilide*,

$$NHPh\cdot CMe_2\cdot CH(CN)\cdot CO\cdot NHPh,$$

glistening leaflets, m. p. 209—210°.

Mesityl oxide behaved similarly towards methyl sodiocyanoacetate, but the *methyl α-cyano-γ-acetyl-ββ-dimethylbutyrate*, $C_{10}H_{15}O_3N$, did not decompose on distillation, b. p. 150—151°/13 mm. It did not condense with ethyl sodiocyanoacetate to form the above acrylyl derivative, and therefore the formation of the latter has to be explained in the following way:

$$CMe_2{:}CH\cdot CO\cdot CH_3 + CH_2(CN)\cdot CO_2Et \rightarrow$$

$$CMe_2{:}CH\cdot CMe{:}C(CN)\cdot CO_2Et \xrightarrow[-EtOH]{+CH_2(CN)\cdot CO_2Et}$$

$$CMe_2{:}CH\cdot CMe{:}C(CN)\cdot CO\cdot CH(CN)\cdot CO_2Et \xrightarrow[-Me_2CO]{+H_2O}$$

(VII) $CMe_2{:}C(CN)\cdot CO\cdot CH(CN)\cdot CO_2Et$.

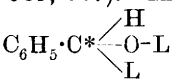
H. *Experiments with ethyl dimethylacrylate.*—This ester only reacted to a slight extent with ethyl sodioacetoacetate, yielding, on distillation of the acid extract, *ethyl* 3 : 5-*diketo*-1 : 1-*dimethyl*cyclo*hexane-2-carboxylate*, $CO<^{CH_2\text{---}CO}_{CH_2\cdot CMe_2}>CH\cdot CO_2Et$, b. p. 160—170°/12 mm.

J. *Action of chloroacetol on ethyl sodioacetoacetate.*—The acid extract of the product in this case yielded a pitch-like mass from which *ethyl α-acetyl-β-ethoxy-β-methylbutyrate*, $OEt\cdot CMe_2\cdot CHAc\cdot CO_2Et$, was isolated by a current of steam, in the form of long, white needles, m. p. 61°. J. C. W.

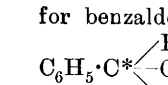
The Supposed Activation of Benzaldehyde by Asymmetric Induction with *d*-Tartaric Acid, as presumed by E. Erlenmeyer. E. Wedekind (*Ber.*, 1914, **47**, 3172—3174).—The interest in Erlenmeyer's so-called asymmetric inductions culminated in the statement that *l*-benzaldehyde could be obtained by the agency of *d*-tartaric acid (A., 1914, i, 967). The active aldehyde was neither distilled nor analysed, however, and the author now shows that the slight activity which benzaldehyde does, indeed, develop is due entirely to an oily condensation product. J. C. W.

The Preparation of Lævorotatory Benzaldehyde by Asymmetric Induction by means of *d*-Tartaric Acid; Conversion of the Same into *l*-Mandelonitrile and *d*-Mandelic Acid. EMIL ERLENMEYER (*Biochem. Zeitsch.*, 1914, **66**, 509—511. Compare A., 1914, i, 967).—The oil produced by the addition of water to the alcoholic solution of benzaldehyde and tartaric acid which has been heated for some hours appears to contain three substances, viz., a small amount of a substance from which *d*-mandelic acid can be produced, and two substances, one neutral and one acid, which can be decomposed into benzaldehyde and tartaric acid. S. B. S.

Stereoisomerism and the Theory of Electrons. H. PAULY (*Biochem. Zeitsch.*, 1914, **67**, 439—442).—The author applies the electronic theory to the explanation of the stereoisomerism of the cinnamic acids and benzaldehyde, lately claimed to have been discovered by Erlenmeyer (A., 1914, i, 965, 967). Instead of the formula



for benzaldehyde, as proposed by Erlenmeyer, the author suggests



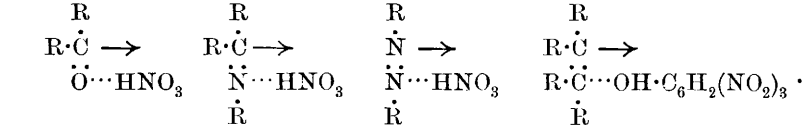
where C* is the asymmetric carbon atom, and –o represents an electron. S. B. S.

Additive Products of Nitric and Picric Acids with Unsaturated Organic Compounds. Constitution of Benzene. G. REDDELIEN (*J. pr. Chem.*, 1915, [ii], **91**, 213—244).—It is generally assumed that the unsaturated oxygen atom of the carbonyl group determines the formation of additive compounds of ketones with acids and salts (compare A., 1912, i, 986), but the author finds that, in general, all compounds containing the group C:O, C:N or N:N yield loose but well-defined additive compounds with nitric acid. Such additive compounds are not obtainable from ethylene derivatives, but the solubility of nitric acid in certain hydrocarbons, for instance, benzylidenefluorene, indicates their existence. Picric acid, which is a strong acid devoid of the oxidising properties, the hygroscopic character and the volatility of nitric acid, forms additive compounds with substances containing the grouping C:O, C:N, N:N or C:C. Picrates of saturated hydrocarbons are unknown, and, in general, aromatic double linkings are far less unsaturated than aliphatic, and their capacity for addition consequently lower; compounds, such as benzene picrate, naphthalene picrate, anthracene picrate, etc., are, however, known, as also are picrates of unsaturated hydroaromatic hydrocarbons, such as pinene.

Additive compounds of nitric acid readily undergo decomposition, even by solvents such as water, with which an equilibrium is attained in dependence on the proportion present. On the other hand, excessively concentrated nitric acid nitrates the organic compound, so that the preparation of the additive compounds necessitates the careful adjustment of the concentration of the acid. Analogous behaviour is

shown by the picrates, a solvent which dissolves one component of a hydrocarbon picrate appreciably more readily than the other effecting either partial or complete scission of the additive compound.

According to Pfeiffer's theory of halochromy (A., 1910, i, 852; 1911, i, 788), the constitution of the additive compounds of nitric and picric acids may be represented thus :



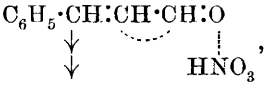
The acid saturates a certain affinity of the atom to which it is juxtaposed, so that some degree of affinity, indicated by the arrow, is liberated at the other atom adjacent to the double linking. Marked modification of the stability of the additive compound is evident where the double linking stands in conjugated relation to a second. If this is a C:O or a C:N group, the stability is diminished. Thus, benzophenone nitrate keeps for half-a-day in a desiccator over sulphuric acid, and fluorenone nitrate for almost two days, whereas benzil nitrate decomposes immediately, and phenanthraquinone nitrate persists for scarcely half-an-hour ; further, additive acid compounds of benzildianil are more unstable than those of benzophenoneanil (A., 1914, i, 695). Where, however, the second double linking is a carbon linking, so that the compound contains the grouping

O:C·C:C, N:C·C:C, or C:C·C:C,

the stability of the additive product is enormously increased. Thus, whilst benzaldehyde nitrate and picrate last only a few hours, the corresponding compounds of cinnamaldehyde remain unchanged for weeks, and similar differences are observed between the additive products of acetophenone and benzophenone, and those of styryl methyl ketone, phenyl styryl ketone, and distyryl ketone (A., 1912, i, 986). The differences of affinity between the groups

O:C·C:O, C:O, and C:C·C:O

may be clearly seen by measuring the extents to which hydrolysis occurs when the nitrates of dibenzoyl, benzophenone, and phenyl styryl ketone are treated with the same proportion of dilute nitric acid at 15°. The constitution of such compounds is best expressed on the basis of Thiele's and Staudinger's views, thus :



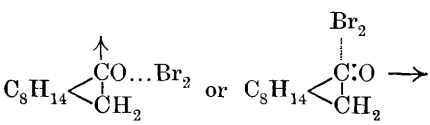
the double arrow denoting an intensified partial valency. Bruni and Tornani's observations (A., 1904, i, 875), and those of Thiele and Henle (A., 1906, i, 571) may be explained similarly, and the slight but distinct power of addition exhibited by benzene, naphthalene and anthracene is also to be attributed to the presence of conjugated double linkings. A constitution similar to that suggested for these picrates has been proposed by Reich (A., 1914, i, 41) for the additive compounds of halogens with unsaturated hydrocarbons.

In order to characterise these additive compounds of nitric and

picric acids and of the halogens as a class of individual substances, the author proposes for them the name "pre-compounds" (Vorver bindungen), signifying thereby molecular compounds,

$$\begin{matrix} A \\ \vdots \\ A \ldots M \end{matrix} \longrightarrow \quad (A = \text{atom}, \ M = \text{molecule}),$$

which arise prior to true saturation of a double linking, but do not necessarily lead to complete saturation and destruction of the double linking. The tendency to addition with formation of pre-compounds seems to be related inversely to the tendency to addition with resolution of the double linking, and it should be possible to isolate molecular halogen additive products with compounds containing C:O or C:N, and perhaps with those containing N:N. Such compounds are, indeed, known, for instance, dibromocamphor (annexed formula), tetrabromobenzylideneazine and azobenzene perbromide, and it may be that the dark perbromides of *pp'*-diethoxystilbene and similar compounds described by Hantzsch and Denstorff (A., 1906, i, 745) are of this nature.



According to Pfeiffer's views, all these pre-compounds should exhibit more or less marked halochromy, and such intensification of colour is always observed. Pfeiffer's investigations on the quinhydrones (A., 1914, i, 551) lead to a third possible structure for the picrates of the hydrocarbons, namely, $OH \cdot C_6H_2(NO_2)_3 \cdot \overset{\uparrow}{\underset{\dot{O}}{N}}:O \ldots C_6H_6$, but such a scheme is incapable of expressing the relations, described above, existing between the additive products of picric and nitric acids and the halogens. Distinct differences apparently exist between the molecular compounds of the nitrohydrocarbons and those of picric acid, owing to the strong acidity of the latter and the feeble acidity of the former. Ostromisslensky (A., 1912, i, 22) gives a fourth structure for the picrates of the hydrocarbons, which, however, leaves unexplained their intense colour.

The pre-compound theory may possess importance in connexion with the problem of orientation in the benzene nucleus. For instance, when benzene is introduced into a mixture of nitric and sulphuric acids, it may be assumed that the benzene and the sulphuric (or nitric) acid first form a pre-compound, free affinities occurring in the ortho- and para-positions to that at which the acid is attached. At these, then, the nitro-group is added, whilst the hydroxyl proceeds to the sulphuric acid and forms water. Treatment with water decomposes the pre-compound with formation of nitro-, dinitro-, and trinitro-benzene.

The view that velocity of reaction = affinity/chemical resistance is applied to the case of benzene and its homologues. The similarity in properties shown by these homologues would indicate that the resistances they offer towards one and the same reagent under definite

conditions would be equal. Benzene, being the initial member of a homologous series, occupies a separate position, but the author shows that it is not necessary to assume the absence of double linkings in the benzene molecule. The latter is discussed in regard to its behaviour towards: (1) Halogens. Luther and Goldberg (A., 1906, ii, 641) have shown that the apparent inactivity of benzene towards halogens is accounted for by the anti-catalytic action of the air and that, in the light, oxygen-free benzene combines almost instantaneously with six atoms of chlorine; towards bromine it shows similar behaviour (private comm. by Luther). As is the case with all compounds containing purely carbon double linkings, these reactions proceed with extreme slowness in the dark. Judged by the attainment of an equilibrium in their reactions with the halogens, various aliphatic double linkings are far more unsaturated than those of benzene. (2) Oxygen. The reaction of benzene with oxidising agents is slow, but not essentially different from that of compounds with aliphatic double linkings. The formation of benzene triozonide and its decomposition into glyoxal (compare Harries and Weiss, A., 1904, i, 861; Harries, A., 1906, i, 225), and the relatively rapid oxidation of benzene by strongly acid permanganate solutions, compared with that of saturated hydrocarbons, such as *cyclo*hexane (compare Wieland, A., 1912, i, 944), indicate the presence of double linkings in the benzene molecule. (3) Hydrogen. The hydrogenation of benzene in presence of metallic catalysts proceeds rapidly and completely if the benzene is absolutely pure, small proportions of thiophen exerting an anti-catalytic effect. Other indications of the presence of double linkings in the benzene molecule are the coloration given with tetranitromethane, the reaction with ethyl diazoacetate, the appearance of a so-called "active" double linking on introduction of a hydroxyl or amino-group, the behaviour towards a mixture of nitric and sulphuric acids, the ability to dissolve up to 3 mols. of hydrogen chloride, the addition of 3 mols. of hypochlorous acid, the molecular refraction, the magnetic rotation in comparison with that of hexatriene, etc. Borsche and Bahr's experimental proof of Kekulé's benzene formula (A., 1914, i, 28) cannot be regarded as valid, as it assumes equality of the chemical resistance in the original and in the monosubstituted compound, which is not justified, since experiments on the chlorination of acetic acid, acetone and toluene, and on the nitration of phenols, etc., show that the chemical resistance is always altered by the entry of a substituent.

Thiele's first formula (A., 1899, i, 554) is regarded as the best expression of the benzene molecule, as it contains the double linkings and pictures the slight, but not suppressed, reactivity. The two objections to this formula, that it should give rise to two isomeric ortho-disubstituted products, and that it does not explain the far greater reactivity of the analogously constructed *cyclo*tetraene, are discussed and answered.

Benzaldehyde nitrate, $C_6H_5\cdot CHO,HNO_3$, is a colourless oil, which remains liquid at $-30°$ and decomposes rapidly in the air, turning yellow and giving up nitric acid. *Acetophenone nitrate*,

$$Ph\cdot COMe,HNO_3,$$

is a colourless oil of similar properties to the preceding compound. Benzophenone nitrate (compare Meyer, A., 1910, i, 179) forms aggregates of thin, yellowish-white prisms, m. p. 31°. *Benzaldehyde picrate*, $C_6H_5\cdot CHO,OH\cdot C_6H_2(NO_2)_3$, forms unstable, pale yellow prisms, m. p. 70—72°, with previous softening. *Cinnamaldehyde picrate*, $CHPh{:}CH\cdot CHO,C_6H_3O_7N_3$, forms pale yellow prisms, m. p. 66—67°. *Distyryl ketone picrate*, $CO(CH{:}CHPh)_2,C_6H_3O_7N_3$, forms stable, orange-coloured, rhombic crystals, m. p. 113—114°. *Benzophenoneanil picrate*, $CPh_2{:}NPh,C_6H_3O_7N_3$, forms deep yellow crystals, m. p. 188—189°. *Fluorenoneanil picrate*, $(C_6H_4)_2C{:}NPh,C_6H_3O_7N_3$, forms oblique, garnet-red prisms, m. p. 187—188°. *Azobenzene nitrate*, $C_6H_5\cdot N_2Ph,HNO_3$, forms highly unstable, red crystals. *Azobenzene picrate* (?) forms unstable, red crystals. *Stilbene picrate* forms unstable, brown needles, m. p. 94—95°. *p* : *p*′-Dimethylstilbene (1 mol.) and picric acid (1 mol.), when fused together, yield brown crystals, which decompose into their components in a few moments. T. H. P.

The Photochemistry of Phenylacetaldehyde; Formation of Triphenylparacetaldehyde and Other Polymerides. Hans Stobbe and Alfred Lippold (*J. pr. Chem.*, 1914, [ii], **90**, 277—296). —Phenylacetaldehyde forms, according to conditions, various polymerisation products. The pure aldehyde was prepared by distillation under reduced pressure of the commercial article. It boiled at 88°/18 mm., and two other fractions of higher boiling point were invariably obtained, which molecular-weight determinations showed to contain partly polymerised products. The mean refractive index of the monomeric aldehyde, $n_C^{20} = 1{\cdot}52204$, was used in subsequent experiments as a criterion of purity, and of the absence of polymerides.

With 23% sulphuric acid a crystalline polymeride, m. p. 155—156°, was produced, which in freezing benzene and chloroform had a molecular weight corresponding with $(C_8H_8O)_3$. Owing to a similarity in properties with paracetaldehyde it is designated *triphenylparacetaldehyde*, and assigned the constitution

$$CH_2Ph\cdot CH\begin{<}O\cdot CH(CH_2Ph)\\O\cdot CH(CH_2Ph)\end{>}O.$$

It is soluble to the extent of 2·7% in the monomeric aldehyde (n_C^{20} of saturated solution = 1·52290). It possesses no aldehydic properties, can be distilled almost without decomposition at 150—160°/0·01 mm., and with slight decomposition at 240—250°/13 mm., but under atmospheric pressure it is depolymerised to the extent of 98·5%.

Concentrated sulphuric acid converts phenylacetaldehyde at ordinary temperatures, and also at −80°, into a resin. Hydrochloric acid (23%) produces in two days a colourless, amorphous non-aldehydic polymeride, and dry hydrogen chloride probably a condensation product; neither of these substances was further investigated. Formic and acetic acids do not cause polymerisation.

Aqueous potassium hydroxide (10%) converts phenylacetaldehyde almost momentarily into a yellowish-white, amorphous mass, which according to molecular-weight determinations in acetic acid is a dimeric modification. It has no aldehydic properties, cannot be crystallised, begins to melt at 50°, and is depolymerised vigorously

at 90—100°, and to the extent of 75% even when distilled in an absolute vacuum. It is designated as *diphenylmetacetaldehyde*, as its properties recall those of metacetaldehyde.

The polymerisation of phenylacetaldehyde in the absence of catalysts leads to two different products, crystalline triphenylparacetaldehyde and a highly refractive viscous substance, the quantity of each depending on the intensity and wave-length of the incident light. In the dark, or with periodical exposure to ultra-violet light, the viscous polymeride, which has a molecular weight at least five times that of the parent substance, is the sole product. In the dark, polymerisation proceeds continuously, but during the exposure to light it appears, from refractive index determinations, to cease; in the succeeding dark period, however, it proceeds again even more rapidly than with specimens which were always kept in the dark. This is therefore an example of photochemical after-effect. An explanation of the retardation during the period of illumination is sought in the conception of two opposing reactions leading to an equilibrium:

$$n\mathrm{C_8H_8O} \underset{\text{light}}{\overset{\text{dark}}{\rightleftharpoons}} (\mathrm{C_8H_8O})_n.$$

At 100° in the dark this polymerisation proceeded with great rapidity, and after twenty-five minutes, a value was obtained for the refractive index which was only reached in twenty days at 21°. By repeated short exposure to light of long wave-length, followed by dark periods, phenylacetaldehyde changed partly into the above polymeride, and partly into triphenylparacetaldehyde, which after some weeks filled the whole liquid with a solid, crystalline mass. Since ultra-violet light had no effect on triphenylparacetaldehyde, it is obvious that the two polymerisations proceed quite independently of each other. In presence of water, the polymerisation is retarded both in the dark and in light of long wave-length. G. F. M.

New Syntheses of Aldehydes. I. Ernst Späth (*Monatsh.*, 1915, **36**, 1—12).—The discovery that one alkyloxy-group of an acetal may be replaced by alkyl or aryl by means of magnesium alkyl or aryl haloids (A., 1914, i, 650) has been extended in the case of ethoxyacetal. This reacts to form two ethers, thus:

$$\mathrm{OEt{\cdot}CH_2{\cdot}CH(OEt)_2 + MgRX \longrightarrow OEt{\cdot}CHR{\cdot}CH_2{\cdot}OEt}$$

and $\mathrm{OEt{\cdot}CHR{\cdot}CH_2{\cdot}OEt + MgRX \longrightarrow CHR{:}CH{\cdot}OEt.}$

These ethers are readily hydrolysed to the same aldehyde, and since ethoxyacetal is easily prepared, the method offers a convenient synthesis even of sensitive aldehydes. The substituted phenylacetaldehydes are described. They all possess fragrant odours.

Some of the organo-magnesium compounds employed displayed remarkable luminescence when exposed to the air. Thus, magnesium *p*-chlorophenyl bromide emits an intense greenish-blue light, and magnesium *o*-4-xylyl bromide a pale yellow.

Ethoxyacetal was prepared from bromoacetal, which was obtained by a simple modification of Freundler and Ledru's method (A., 1905, i, 326). The latter was added to a cold concentrated solution of sodium ethoxide and then heated at 100° for a day. The ethoxyacetal was

boiled with sodium and then had b. p. 57—58°/11 mm. In general the preparation of the aldehydes was carried out by adding ethoxyacetal to the Grignard reagent, heating the mixture in a metal-bath under reflux (allowing the solvent ether to escape), decomposing the product by dilute hydrochloric or acetic acid, isolating and distilling the mixed ethers, and allowing these to drop into boiling, about 50% sulphuric acid at such a rate that the products distilled over in the steam. The aldehydes were isolated from the ethereal extract of this distillate by means of sodium hydrogen sulphite and the unchanged ethers submitted to hydrolysis again.

Ethoxyacetal reacts with magnesium phenyl bromide or iodide to form *αβ*-diethoxy-*α*-phenylethane and also phenylvinyl ethyl ether, both of which yield phenylacetaldehyde on hydrolysis. Similarly, magnesium *o*-tolyl iodide yields a little *o*-tolylvinyl ethyl ether, b. p. 103—106°/10 mm., and also *αβ-die hoxy-α-o-tolylethane*,

$$C_6H_4Me\cdot CH(OEt)\cdot CH_2\cdot OEt,$$

b. p. 119—121°/9 mm., both of which give *o*-tolylacetaldehyde on hydrolysis (Kronik, A., 1911, i, 210). *m*-Iodotoluene was transformed into m-*tolylacetaldehyde*, b. p. 94°/10 mm., and *p*-bromotoluene into *αβ-diethoxy-α*-p-*tolylethane*, b. p. 120—122°/10 mm., and then into *p*-tolylacetaldehyde (Kling, A., 1908, i, 188). 4-Iodo-*m*-xylene yielded o-p-*dimethylphenylacetaldehyde*, b. p. 106—108°/10 mm., and *p*-chlorobromobenzene gave *αβ-diethoxy-α*-p-*chlorophenylethane*, $C_8H_7Cl(OEt)_2$, b. p. 126—129°/9 mm., and then p-*chlorophenylacetaldehyde*, b. p. 104—106°/10 mm.

Attempts were also made to prepare chlorohydrins by the interaction of chloroacetaldehyde with magnesium alkyl or aryl haloids and to convert these into glycol ethers and then into aldehydes, but in most cases ethylene oxides were obtained. Chloroacetaldehyde was obtained by distilling the pure trimeride, b. p. 142—144°/10 mm. This formed *β*-chloro-*α*-phenylethyl alcohol, b. p. 112—114°/10 mm., with magnesium phenyl bromide, and this yielded mainly styrene oxide with a small quantity of *β*-ethoxy-*α*-phenylethyl alcohol, b. p. 118—120°/11 mm., when warmed with sodium ethoxide. The latter substance was converted into phenylacetaldehyde by the above method. A somewhat better result was obtained in the case of 4-bromo-*o*-xylene. This yielded o-4-*xylylethylene oxide*, $C_{10}H_{12}O$, b. p. 105—108°/10 mm., and also a fair amount of *β-methoxy-α-o-4-xylylethyl alcohol*,

$$C_6H_3Me_2\cdot CH(OH)\cdot CH_2\cdot OMe,$$

b. p. 144—149°/10 mm. (sodium methoxide was used in this case). The latter yielded o-4-*xylylacetaldehyde*, b. p. 112—114°/10 mm., on hydrolysis. *p*-Chlorobromobenzene only yielded p-*chlorophenylethylene oxide*, C_8H_7OCl, b. p. 102—103°/10 mm. J. C. W.

Alkyl-, Oximino-, and Amino-derivatives and Diketones of the *cyclo*Hexane Series. I. Derivatives of Methyl*cyclo*hexan-3-one. A. Kötz, E. Nussbaum, and E. Takens (*J. pr. Chem.*, 1914, [ii], **90**, 357—381).—Kotz and Blendermann (A., 1913, i, 1069) and Kötz and Lemien (this vol., i, 247) have shown that *β*-ketone-oxalic esters may be alkylated by way of their sodium derivatives, and Kotz and Schwarz (*Diss.*, Göttingen, 1908) found that the velocity of

substitution of the characteristic hydrogen atom in cyclic β-ketone-carboxylic esters diminishes considerably from methyl to ethyl to *iso*propyl. Study of the action of allyl and propyl iodides on ethyl sodio-β-methyl*cyclo*hexanonecarboxylate shows that of the three alkyl haloids containing three carbon atoms, the unsaturated compound exhibits the greatest, and the saturated normal-chain compound the least reactivity.

Ketonic decomposition of the 1-methyl-4-alkyl-3-*cyclo*hexanone-4-carboxylic esters proceeds most easily with the 4-methyl- and somewhat less readily with the 4-ethyl-derivative, and of the allyl- *iso*propyl- and propyl-derivatives the first is most and the last least easily decomposed.

Alcoholysis of 1-methyl-4-allyl-3-*cyclo*hexanone-4-carboxylic esters and of the corresponding 1-methyl-4-propyl esters leads to ethyl β-methyl-ε-allylpimelate and β-methyl-ε-propylpimelate, the acid corresponding with the former of these being the carboxyl derivative of the higher homologue of citronellic acid or of the menthonenic acid, $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H$, obtained by Wallach ("Terpene und Campher," 1914, 382) from menthonitrile.

2 : 4-Dioximino-1-methyl-3-*cyclo*hexanone, obtained by von Baeyer (A., 1896, i, 445) as a by-product of the nitrosation of pulegone, has been prepared by treatment of 1-methyl-3-*cyclo*hexanone with amyl nitrite and acetyl chloride (compare Borsche, A., 1910, i, 178).

Ethyl 1-*methyl*-4-*allyl*-3-cyclo*hexanone*-4-*carboxylate*, $C_{13}H_{20}O_3$, prepared by the action of sodium ethoxide and allyl iodide on ethyl 1-methyl-3-*cyclo*hexanone-4-carboxylate, is a pale yellow oil, b. p. 258—260°, or 128—130°/9 mm., and forms a *semicarbazone*, $C_{14}H_{23}O_3N_3$, m. p. 153—154°. When reduced by Skita's method, it yields *ethyl* 1-*methyl*-4-*propyl*-3-cyclo*hexanone*-4-*carboxylate*, $C_{13}H_{22}O_3$, b. p. 263—265°, or 145—150°/20 mm., which may also be obtained by the action of propyl iodide on the potassium derivative of ethyl 1-methyl-3-*cyclo*hexanone-4-carboxylate, and forms a *semicarbazone*, m. p. 158—159°.

With alcoholic potassium hydroxide, ethyl 1-methyl-4-allyl-3-*cyclo*hexanone-4-carboxylate gives 1-methyl-4-allyl-3-*cyclo*hexanone, b. p. 211—214° (Augspurger, *Diss.*, Göttingen, 1913, gave 195—220°), which forms a semicarbazone, m. p. 147—149°; reduction of the ketone yields 1-methyl-4-*n*-propyl-3-*cyclo*hexanone, the semicarbazone of which has b. p. 157—158° (Augspurger, *loc. cit.*, gave 157—161°). Treatment of the 4-allyl ester with sodium ethoxide at 150° gives *ethyl β-methyl-ε-allylpimelate*,

$$CH_2{:}CH{\cdot}CH_2{\cdot}CH(CO_2Et){\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2Et,$$

b. p. 175—178°/20 mm., and this on reduction yields *ethyl β-methyl-ε-propylpimelate*, b. p. 163—164°/12 mm.

4-Oximino-1-methyl-3-*cyclo*hexanone (compare Takens, *Diss.*, Göttingen, 1910), m. p. 158—159°, forms a *benzoyl* derivative, $C_{14}H_{15}O_3N$, m. p. 115°, and on reduction with stannous chloride and hydrochloric acid is converted into 4-amino-1-methyl-3-*cyclo*hexanone, which forms a *hydrochloride*, $C_7H_{13}ON,HCl$, m. p. 171°, a *carbamide*, $C_8H_{14}O_2N_2$, m. p. 230°, and a *benzoyl* derivative, $C_{14}H_{17}O_2N$, m. p. 118°. When the hydrochloride of this amino-ketone is neutralised with alkali hydroxide

or carbonate solution, it undergoes condensation to the *pyrazine base*, $CHMe\cdot CH_2\cdot C{:}N{-}CH\cdot CH_2\cdot CH_2$ / $CH_2\cdot CH_2{-}CH\cdot N{:}C\cdot CH_2{-}CHMe$, m. p. about 75°, which is difficult to purify.

1-Methyl-3 : 4-*cyclo*hexanedionephenylosazone, obtained by the action of phenylhydrazine on 4-oximino-1-methyl-3-*cyclo*hexanone, has m. p. 140° (compare Sauer, *Diss.*, Göttingen, 1914).

2 : 4-*Dioximino*-1-*methyl*-3-cyclo*hexanone*,

$$OH\cdot N{:}C\langle \begin{matrix} CO\cdot C(:NOH) \\ CH_2{-}CH_2 \end{matrix} \rangle CHMe,$$

prepared by the action of acetyl chloride and amyl nitrite on either 1-methyl-3-*cyclo*hexanone or 4-oximino-1-methyl-3-*cyclo*hexanone, begins to turn brown at 170°, and is decomposed completely at 190°. When the methylhexanone is employed, rapid addition of the amyl nitrite or the initial presence of too much acetyl chloride leads to the formation of the hydrochloride of the methyl*cyclo*hexenylidenemethyl*cyclo*hexanone,

$$CH_2\langle \begin{matrix} CHMe\cdot CH_2 \\ CH_2{-}CH_2 \end{matrix} \rangle C{:}C\langle \begin{matrix} CH_2\cdot CH_2 \\ CO{-}CH_2 \end{matrix} \rangle CHMe,$$

m. p. 90°.

2 : 4-*Diamino*-1-*methyl*-3-cyclo*hexanone*, $C_7H_{14}ON_2$, obtained by reduction of 2 : 4-dioximino-1-methyl-3-*cyclo*hexanone, gives a *hydrochloride* ($+2HCl$), m. p. about 270°.

3 : 4-*Dioximino*-1-*methyl*cyclo*hexane*, $C_7H_{12}O_2N_2$, prepared from hydroxylamine and 4-oximino-1-methyl-3-*cyclo*hexanone, has m. p. 168°, and in alcoholic solution gives brown precipitates with copper and iron salts, a reddish-violet precipitate with nickel nitrate, and a deep red coloration with cobalt salts. The *nickel* salt,

$$\begin{matrix} CHMe\cdot CH_2\cdot C{:}NO \\ CH_2{-}CH_2{-}C{:}NO \end{matrix} \rangle Ni\langle \begin{matrix} N(OH){:}C\cdot CH_2\cdot CHMe \\ N(OH){:}C\cdot CH_2\cdot CH_2 \end{matrix},$$

detonates when heated.

3 : 4-*Diamino*-1-*methyl*cyclo*hexane*, obtained by reduction of the dioximino-compound, is a liquid and forms a *hydrochloride*, m. p. above 300°, a yellow *platinichloride*, $C_7H_{16}N_2,H_2PtCl_6$, m. p. above 300°, and a *dibenzoyl* derivative, m. p. 162°.

1-*Methyl*-3 : 4-cyclo*hexanedione*, $C_7H_{10}O_2$, prepared from 4-oximino-1-methyl-3-*cyclo*hexanone or 3 : 4-dioximino-1-methyl*cyclo*hexane, has m. p. 35—36°, b. p. 85°/12 mm., gives a red coloration with ferric chloride in alcoholic solution and reacts in its enolic form with sodium, hydrogen being evolved. Its phenylosazone is described above, and its *dioxime*, which may also be obtained from 4-oximino-1-methyl-3-*cyclo*hexanone (*vide supra*), yields a *dibenzoyl* derivative, m. p. 171°.

T. H. P.

The Influence of the CO-Group on the Mobility of the Chlorine Atom in 4-Chloro-3-nitrobenzophenone and 4 : 4′-Dichloro-3 : 3′-dinitrobenzophenone. D. Maron and Charles Fox (*Ber.*, 1914, **47**, 2774—2783).—By successive action of phosphorus pentachloride and aluminium chloride on a mixture of 4-chloro-3-nitrobenzoic acid and benzene (compare Ullmann and Mallet, A., 1898, i, 594), there was obtained 4-*chloro*-3-*nitrobenzo*-

phenone, $COPh\cdot C_6H_3Cl\cdot NO_2$, as colourless needles, m. p. 105°; this was converted by reduction with iron and acetic acid into 4-*chloro*-3-*aminobenzophenone*, colourless needles, m. p. 94°; *acetyl* derivative, needles, m. p. 79—81°. When 4-chloro-3-nitrobenzophenone was heated under increased pressure at 124—128° with alcoholic ammonia and sodium acetate, interaction took place with formation of 3-nitro-4-aminobenzophenone, the observed m. p., 140·5°, being higher than that recorded previously (Schöpff, A., 1892, i, 337); *benzoyl* derivative, colourless leaflets, m. p. 154—155°; *acetyl* derivative, very pale yellow needles. Treatment of the chloronitro-compound with aniline at water-bath temperature yielded 3-nitro-4-anilinobenzophenone, m. p. 157°, whilst an alcoholic solution of dimethylamine at 110—170° yields 3-*nitro*-4-*dimethylaminobenzophenone*, golden-yellow needles, m. p. 116°.

4-*Chloro*-3-*nitro*-2′ : 4′-*dimethylbenzophenone*, obtained by the successive action of phosphorus pentachloride and aluminium chloride on a suspension of 4-chloro-3-nitrobenzoic acid in *m*-xylene, reacted with an alcoholic solution of dimethylamine in the presence of sodium acetate at 100°, producing 3-*nitro*-4-*dimethylamino*-2′ : 4′-*dimethylbenzophenone*, deep yellow needles, m. p. 103—104°.

In the general manner a *dichloro*-3-*nitromethylbenzophenone* was prepared from 4-chloro-3-nitrobenzoic acid and *p*-chlorotoluene; the m. p., 113—118°, was not sharp, and it is probable that the product was a mixture of the two possible isomerides.

4 : 4′-*Dichloro*-3-*nitrobenzophenone*, obtained in the usual manner from 4-chloro-3-nitrobenzoic acid and chlorobenzene, formed colourless needles, m. p. 88—89°; nitration converted this into 4 : 4′-*dichloro*-3 : 3′-*dinitrobenzophenone*, pale yellow needles, m. p. 132—133°, which when heated with alcoholic ammonia and sodium acetate at 122—127° yielded 3 : 3′-*dinitro*-4 : 4′-*diaminobenzophenone*, red needles, m. p. 287—289°; *diacetyl* derivative, yellow needles, m. p. 219—221°.

1-Chloro-2 : 4-dinitrobenzene and 4-chloro-3-nitrobenzophenone on treatment with potassium xanthate yielded respectively tetranitrodiphenyl disulphide and a *dinitrodibenzoyldiphenyl sulphide*,

$$(NO_2\cdot C_6H_3Bz_2)_2S,$$

m. p. 174—175°. On heating at 100° for an hour, a mixture of 4 : 4′-dichloro-3-nitrobenzophenone, sodium acetate, and potassium xanthate in alcoholic solution, the product was a *dinitrodichlorobenzoyldiphenyl sulphide*, $[C_6H_4Cl\cdot CO\cdot C_6H_3(NO_2)]_2S$, yellow needles, m. p. 205—206°. D. F. T.

Preparation of ω-Aminoresacetophenone. S. Keimatsu and S. Nakahashi (*J. Pharm. Chim.*, 1915, [vii], **11**, 136; from *Yakugakuzasshi*, 1914).—Resacetophenone is converted by the action of amyl nitrite and sodium ethoxide into oximinoresacetophenone, m. p. 160°, which gives *ω-aminoresacetophenone* when treated with zinc chloride or reduced catalytically. The substance may be crystallised from acetone in the form of long, light yellow needles, m. p. 198° (decomp.); it yields a *triacetyl* derivative, $NHAc\cdot CH_2\cdot CO\cdot C_6H_3(OAc)_2$, colourless prisms, m. p. 136—137°, a *phenylhydrazone*, m. p. 195—196°, a *hydrochloride* (colourless needles), m. p. 250°, and a *picrate* (yellow

needles), m. p. 188° (decomp.). Unlike other amino-ketones, ω-aminoresacetophenone is stable in the free state. W. P. S.

Determination of Constitution of Enols. III. The Behaviour of the Desmotropic Formyldeoxybenzoins towards Ozone. JOHANNES SCHEIBER and GEORG HOPFER (*Ber.*, 1914, **47**, 2704—2708).—Formyldeoxybenzoin exists in two enolic forms, the existence of which might be due to geometrical isomerism, but for which Wislicenus and Ruthing (A., 1911, i, 303) prefer the structural isomeric formulæ CPhO·CPh:CH·OH and OH·CPh:CPh·CHO respectively. The chemical behaviour of these substances, however, does not exclude the possibility that they are actually geometrical isomerides, and to decide this point they have been submitted to the action of ozone. If the yellow α-isomeride possesses the former of the above formulæ, its ozonide should give rise to benzil and formic acid as fission products, whilst the β-isomeride on the basis of the second structure might be expected to yield phenylglyoxal and benzoic acid.

When put to the test of experiment by treating with ozone a solution of the α-isomeride or a suspension of the β-isomeride in carbon tetrachloride at −20°, the same products were obtained in both cases, namely, benzil and formic acid, so that in all probability the α- and β-compounds are truly geometrical isomerides having the former of the above structures.

Determination of the percentage of the enolic dynamic isomeride in each of the above compounds by K. H. Meyer's titration method indicated approximately 101% and 95% of enol in the α- and β-isomerides respectively. D. F. T.

α-Chloro- and -Bromo-substitution Products of αα′-Unsaturated Ketones. THEODOR HELLTHALER (*Annalen*, 1914, **406**, 151—173).—The author has investigated the substitution products obtained from the additive compounds of the halogens and αα′-unsaturated ketones by the elimination of hydrogen haloid by means of pyridine or anhydrous alkali acetate. In most cases an α-halogen substituted product is obtained, but 2 : 5-dibenzylidene-*cyclo*pentanone tetrabromide loses the whole of its halogen, the original, unsaturated cyclic ketone being regenerated.

By boiling during one hour an absolute alcoholic solution of phorone tetrabromide and anhydrous potassium acetate (4 mols.), nearly 76% of the halogen is removed, but when the time of boiling and the amount of the acetate are diminished by one-half, *αα′-dibromophorone*, $(CMe_2{:}CBr)_2CO$, faintly yellow prisms, m. p. 30°, is obtained. It does not react additively with bromine or hydrogen bromide, and is oxidised by aqueous sodium carbonate and potassium permanganate, yielding acetone, oxalic acid, and a little acetic acid.

In a similar manner, *phorone tetrachloride*, $CO(CHCl{\cdot}CMe_2Cl)_2$, colourless prisms, m. p. 59°, prepared from its constituents in carbon tetrachloride at 0°, yields *αα′-dichlorophorone*, $C_9H_{12}OCl_2$, b. p. 105—106°/15 mm.

Distyryl ketone dibromide (Groebel, A., 1903, i, 497) is converted by boiling ethyl-alcoholic sodium acetate into *β-bromodistyryl ketone*, CHPh:CBr·CO·CH:CHPh, pale yellow, prismatic needles, m. p. 66°. This substance is scarcely affected by boiling with pyridine or with sodium acetate and acetic anhydride, reacts with bromine in carbon tetrachloride to form *bromodistyryl ketone dibromide*,

CHPh:CBr·CO·CHBr·CHPhBr,

prismatic needles, m. p. 121° (decomp.), at 0°, and *tetrabromide*, CHPhBr·CBr_2·CO·CHBr·CHPhBr, colourless prisms, m. p. about 184° (decomp.), at the ordinary temperature (with 2 mols. of bromine), and reacts with boiling methyl-alcoholic potassium hydroxide (1 mol.) to form cinnamoylacetophenone.

Di-β-bromostyryl ketone, $CO(CBr:CHPh)_2$, yellow, prismatic needles, m. p. 97—97·5°, can be prepared from the preceding bromides, but is best obtained by boiling distyryl ketone tetrabromide with alcoholic sodium acetate or with pyridine. It is not attacked by boiling aqueous potassium permanganate, alcoholic ammonia, pyridine, or boiling acetic anhydride and sodium acetate, loses hydrogen bromide by treatment with phenylhydrazine or aniline in ethereal solution, and is reduced by amorphous phosphorus and boiling hydriodic acid, D 1·7, yielding 1 : 2-diphenyl*cyclo*pentane (Japp and Lander, T., 1897, **71**, 128). A cyclic structure for di-β-bromostyryl ketone is excluded, because the ketone in acetone solution at 0° is oxidised by potassium permanganate, yielding benzaldehyde, benzoic acid (impure), and oxalic acid.

By reaction with bromine in carbon tetrachloride, di-β-bromostyryl ketone yields *dibromodistyryl ketone dibromide*.

CHPhBr·CBr_2·CO·CBr:CHPh,

colourless plates, m. p. 184° (decomp.), which does not react with bromine or phosphorus pentabromide.

Di-β-chlorostyryl ketone, $CO(CCl:CHPh)_2$, colourless plates, m. p 111—112°, is obtained from distyryl ketone tetrachloride and alcoholic sodium acetate. In a similar manner or by treatment with pyridine, di-*p*-methoxystyryl ketone tetrabromide yields *di-β-bromo-p-methoxystyryl ketone*, $CO(CBr:CH·C_6H_4·OMe)_2$, yellow, monoclinic prisms, m. p. 101°. C. S.

The Isomerism of the Hydrojuglones. Richard Willstätter and Alvin S. Wheeler (*Ber.*, 1914, **47**, 2796—2801).—No doubt exists as to the constitution of juglone, which has for many years been recognised as 8-hydroxy-1 : 4-naphthaquinone, but the nature of the two isomeric hydrojuglones has been less satisfactorily explained. Mylius (A., 1885, 169, 803; 1886, 69) isolated the two isomerides from green walnut shells, and observed that the less easily fusible α-compound was probably a true quinol, being easily oxidised to juglone, whilst the β-isomeride could not be directly oxidised to juglone; the α- and β-compounds, however, were interconvertible, the change $\alpha \rightarrow \beta$ being effected by distillation or by hydrolysis of the acyl derivatives, whilst the transformation $\beta \rightarrow \alpha$ occurred on treatment with alcoholic-aqueous hydrochloric acid. The isomerism was explained by Mylius as of the

ordinary position-isomerism type, but the easy interconvertibility appears to conflict with this.

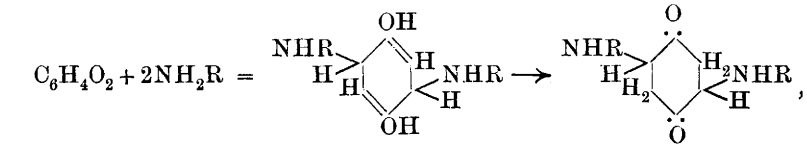
It is now found that if α-hydrojuglone is merely melted, an equilibrium mixture containing almost 75% of the β-compound is produced, whilst an alkaline solution of the β-isomeride (in the absence of air) on acidification regenerates the α-compound. These phenomena are those of keto-enol isomerism, and further experiment confirms this view. α-Hydrojuglone, the solution of which gives a more marked fluorescence, is, therefore, 1 : 4 : 8-trihydroxynaphthalene, whilst β-hydrojuglone is a ketonic form :

$$OH\cdot C_6H_3\langle \begin{matrix} CO\text{———}CH \\ \| \\ CH(OH)\text{–}CH \end{matrix}, \text{ or } OH\cdot C_6H_3\langle \begin{matrix} CO\text{——}CH_2 \\ | \\ C(OH){:}CH \end{matrix}.$$

This is the first case of keto-enol isomerism with a phenol of the naphthalene group.

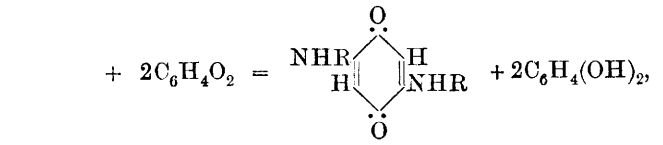
The preparation of juglone was found to be most conveniently effected by oxidation of 1 : 5-dihydroxynaphthalene by sodium dichromate and dilute sulphuric acid ; oxidation can also be performed in benzene solution with lead dioxide. α-Hydrojuglone, whether obtained by reduction of juglone, by rearrangement of the β-isomeride, or by isolation from unripe walnuts, was found to have m. p. 148°, whereas Mylius recorded 168—170° ; the most convenient reducing agent for juglone was zinc dust and 2*N*-sulphuric acid, the juglone being in ethereal solution. β-Hydrojuglone, hexagonal tablets, m. p. 96—97°, was convertible into a *semicarbazone*, prismatic needles, m. p. 197—198° (decomp.), a *phenylsemicarbazone*, needles, decomp. at 243°, and an *oxime*. D. F. T.

Action of the Three Isomeric Aminobenzoic Acids on Benzo-, Tolu- and *p*-Xylo-quinones. Otto Suchanek (*J. pr. Chem.*, 1914, [ii], **90**, 467—490).—The author has extended the work of Ville and Astre (A., 1895, i, 465, 533) and finds that *p*-benzoquinone and its homologues form additive products with the three aminobenzoic acids and with their esters, 1 mol. of the quinone always uniting with 2 mols. of the acid. This proportion is in agreement with Posner's theory (A., 1904, i, 1029), which is based on a modification of Thiele's partial valency formula. The additive compounds are readily soluble, crystallisable substances, which are easily converted by oxidation into the corresponding substitution products, the anilinoquinones, and by reduction into the quinols. The author regards them as invariable intermediate products in the formation of the anilinoquinones in aqueous or alcoholic solution, the two phases of the reaction being as follows : (1) Formation of the enolic additive compound and its transformation into the stable keto-form :

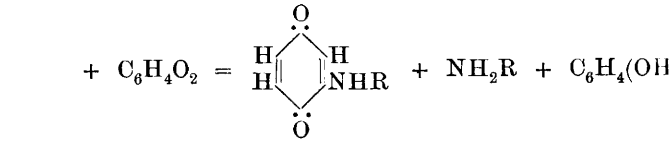


the formation of which is shown by intense reddening of the solution.

(2). Oxidation of the additive compounds by quinone to either (*a*) the dianilinoquinones:



or (*b*) monoanilinoquinones,



In both aqueous and alcoholic solutions, reactions (*a*) and (*b*) proceed simultaneously.

According to Posner (*loc. cit.*), the formula of a quinone contains two separate systems of conjugated double linkings, to which the amine molecules are added with displacement of the double linkings. The two formulæ for toluquinone possible according to this theory should give rise to two different series of additive products, but only in one of these would oxidation lead to a *p*-dianilinotoluquinone, the other yielding a *p*-monoanilinoquinone. Although substitution products of both series are known, only toluquinonemonoaminobenzoic acids are obtainable by the interaction of toluquinone and the aminobenzoic acids. With *p*-xyloquinone, two series are also possible, but the author finds that only the additive compounds and not the mono- or di-aminobenzoic acids are formed. These results are in complete agreement with Posner's theory and with Suida's experiments on the dyeing of animal fibres by quinones (A., 1913, i, 779).

The additive compounds are unstable towards reducing or dissociating agents, and they may be titrated with either iodine or titanium chloride. They are decomposed into their components by concentrated acid or alkali and also by heating, the volatile quinone then subliming. Their melting points are higher for the para- than for the ortho-compounds, and they rise as the molecular weight diminishes.

The additive *compound* of benzoquinone with *p*-aminobenzoic acid, $C_6H_4O_2,2NH_2\cdot C_6H_4\cdot CO_2H$, forms long, ruby-red needles, m. p. 380—381° (in a sealed tube containing carbon dioxide), and when oxidised with hydrogen peroxide yields *p*-benzoquinone-2 : 5-di-*p*-aminobenzoic acid (*vide infra*). That with *o*-aminobenzoic acid,

$$C_6H_4O_2,2NH_2\cdot C_6H_4\cdot CO_2H,$$

forms drusy masses of red, monoclinic crystals, with metallic green fracture, m. p. 210° (in sealed tube); when left for a long time it becomes colourless, the quinone volatilising.

The compound of toluquinone with *p*-aminobenzoic acid,

$$C_6H_3MeO_2,2NH_2\cdot C_6H_4\cdot CO_2H,$$

forms bundles of dark red needles, m. p. 176°. The *methyl* ester forms cinnabar-red crystals, m. p. 46°. The di-*o*-aminobenzoic acid *compound*,

$C_6H_3MeO_2,2NH_2\cdot C_6H_4\cdot CO_2H$, forms peach-blossom red, rhombic crystals, m. p. 129°.

The additive *compound* of *p*-xyloquinone with *o*-aminobenzoic acid, $C_6H_2Me_2O_2,2NH_2\cdot C_6H_4\cdot CO_2H$, forms ruby-red, monoclinic crystals, m. p. 107—108°.

The benzoquinonediaminobenzoic acids dissolve in concentrated sulphuric or nitric acid, giving blood-red solutions and in dilute ammonia or alkali carbonate solution giving deep red solutions of the corresponding salts. They do not melt but char on ignition, and, when reduced by means of tin and hot concentrated hydrochloric acid, yield the unstable quinoldianilinodicarboxylic acids, which could not be isolated.

p-*Benzoquinone*-2:5-*di*-p-*aminobenzoic acid*, $C_6H_2O_2(NH\cdot C_6H_4\cdot CO_2H)_2$, forms brown needles or plates with a violet tint. Its *silver* salt ($+2H_2O$), which carbonises without melting, its *barium* salt, and its *ethyl* ester, which forms long, brownish-yellow needles, m. p. 280°, were prepared.

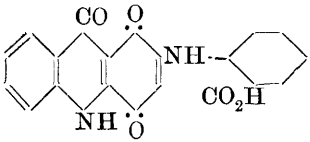
p-*Benzoquinone*-2 : 5-*di*-m-*aminobenzoic acid*, $C_{20}H_{14}O_6N_2$, forms long, lanceolate prisms. Its *silver* salt ($+2H_2O$) remains unmelted at 350°.

p-*Benzoquinone*-2 : 5-*di*-m-*acetylaminobenzoic acid*,

$$CO_2H\cdot C_6H_4\cdot NAc\cdot C_6H_2O_2\cdot NAc\cdot C_6H_4\cdot CO_2H,$$

forms microscopic needles, which carbonise without melting.

p-Benzoquinone-2-*p*-aminobenzoic and -2-*m*-aminobenzoic acids remain unmelted at 400°. They form brown solutions in concentrated sulphuric acid and, on reduction by means of tin and hydrochloric acid, yield the hydroxylic compounds, which rapidly oxidise.



1 : 4 : 5-*Triketoacridine*-3-o-*aminobenzoic acid* (annexed formula), obtained by heating *p*-benzoquinonedi-*o*-aminobenzoic acid (compare Ville and Astre, *loc. cit.*) with concentrated sulphuric acid, forms an ochre-yellow, crystalline precipitate, which does not melt and gives a reddish-brown solution in concentrated sulphuric acid.

2-*Toluquinone*-5-o-*aminobenzoic acid*, $CH_3\cdot C_6H_2O_2\cdot NH\cdot C_6H_4\cdot CO_2H$, forms brownish-violet needles, m. p. about 283° (in sealed tube).

Ethyl 2-*toluquinone*-5-p-*aminobenzoate*, $CH_3\cdot C_6H_2O_2\cdot NH\cdot C_6H_4\cdot CO_2Et$, prepared from toluquinone and ethyl *p*-aminobenzoate, forms violet plates, m. p. 175—176°. The corresponding *acid*, $C_{14}H_{11}O_4N$, forms brown crystals remaining unmelted at 350°. T. H. P.

Anilinoquinones. Action of α-Naphthaquinone on *p*-, *m*-, and *o*-Aminobenzoic Acids. Rudolf Hauschka (*J. pr. Chem.*, 1914, [ii], **90**, 447—466).—In view of the fact that Suida (A., 1913, i, 779) and also Scharvin (A., 1913, i, 661) have expressed the view that the dyeing of wool is to be attributed to the action of the quinonoid group of the dye on the active amino-groups of the proteins, the interaction of quinones and amino-acids acquires new importance. By the action of α-naphthaquinone on *o*-, *m*-, and

p-aminobenzoic acids, the author obtains only monoanilinoquinones under the most varying experimental conditions, whereas Ville and Astre (A., 1895, i, 465, 533) and Astre and Stévignon (A., 1897, i, 525) found that, from *p*-benzoquinone and trichloro-*p*-benzoquinone on the one hand and *o*-aminobenzoic and *o*-aminocinnamic acids on the other, dianilinoquinones and dianilinoquinoneanils are preferably formed. The fact that monoanilinoquinones are formed only rarely in the benzene series, whereas they are the only anilinoquinones known in the naphthalene series, depends on steric hindrance. Two molecules of an amine never enter the molecule of a benzoquinone in the ortho-position, whilst in α-naphthaquinone only the neighbouring 2- and 3-positions are available, so that monoanilinonaphthaquinones are the only ones possible Additive compounds such as are often formed in the interaction of benzoquinones and amines are not obtained in the naphthalene series.

The reaction between α-naphthaquinone and *p*-aminobenzoic acid proceeds best in the cold and when the proportions are 2 mols. of the quinone to 1 mol. of the amino-acid, but it is not complete at the end of five months. The reaction is somewhat accelerated and the consumption of the quinone considerably diminished by the presence of an oxidising agent, such as hydrogen peroxide. With none of the three amino-acids could a dianilinoquinone or a quinoneanil be obtained.

α-*Naphthaquinone*-2-p-*aminobenzoic acid*,

$$C_{10}H_5O_2\cdot NH\cdot C_6H_4\cdot CO_2H,$$

exists in three modifications, obtained by varying the conditions of the reaction or of the subsequent crystallisation: (1) orange-yellow or bronze, rhombic needles with marked metallic lustre, which undergo partial sublimation at 250°, and melt at 319° in a sealed tube containing carbon dioxide; reduction by means of titanium chloride and hydrochloric acid in acetic acid solution yields the *leuco*-compound, α-*naphthaquinol*-2-p-*aminobenzoic acid*, in colourless needles, which immediately redden in the air. (2) Purple-red, triclinic leaflets or flocks, which are converted into form (1) at 178°. (3) Ruby-red, rhombic needles, which are transformed into form (1) at 250—280°. The acid may be titrated with titanium chloride, ammonium thiocyanate being used as indicator. The following salts were analysed: *barium*, $+5H_2O$, which begins to decompose at 250°; *silver*, $+H_2O$, m. p. 323—324°, and *ammonium*, $+xH_2O$, m. p. 304°, and the *calcium* (decomp. 270°), *magnesium* (decomp. 256°), *aluminium* (not melted at 400°), *ferrous*, *ferric*, *copper*, *lead* (not melted at 400°), *tin*, *mercury*, and *sodium* salts prepared. Its *ethyl* ester has m. p. 185°, or 189° in a sealed tube, and its *methyl* ester, m. p. 232—233°, or 239° in a sealed tube.

α-*Naphthaquinone*-2-p-*acetylaminobenzoic acid*,

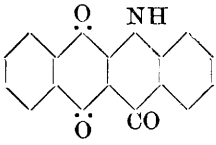
$$C_{10}H_5O_2\cdot NAc\cdot C_6H_4\cdot CO_2H,$$

forms a dark red, crystalline precipitate, m. p. 310°. When treated with concentrated sulphuric acid and mercury, α-naphthaquinone-2-*p*-aminobenzoic acid is oxidised to phthalic acid.

α-*Naphthaquinone*-2-m-*aminobenzoic acid*, $C_{17}H_{11}O_4N$, forms brick-red or wine-red flocks or ruby-red needles, m. p. 254°, and exhibits

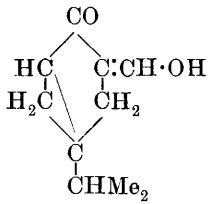
chemical behaviour completely analogous to that of the para-isomeride. Its *barium* ($+4H_2O$) and *silver* ($+4H_2O$) salts were prepared.

α-Naphthaquinone-2-o-aminobenzoic acid, $C_{17}H_{11}O_4N$, forms irregular, orange-red leaflets or needles, m. p. 265°, and, in general, forms more readily soluble derivatives than its isomerides. Its reduction by means of titanium chloride is accompanied by initial blackening of the solution, owing to the formation of quinhydrone-like products, which are also formed to less extents with the para- and meta-isomerides. Its *barium* ($+H_2O$) and *silver* salts ($+H_2O$) were prepared.



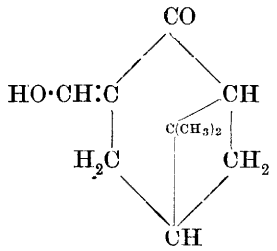
1 : 4-*Naphthaquinoneacridone* [1 : 6 : 7-*Triketo-ββ-phenonaphthacridine*] (annexed formula), prepared by the anhydridation of the preceding compound by means of concentrated sulphuric acid, forms yolk-yellow needles, m. p. about 350°, and is indifferent to the action of acids or alkalis. T. H. P.

Synthesis of Terpene Ketones, $C_{10}H_{16}O$, from Ketones, $C_9H_{14}O$. A. Kötz and E. Lemien (*J. pr. Chem.*, 1914, [ii], **90**, 314—317).—Ketones of the terpene series, $C_9H_{14}O$, such as sabinaketone, nopinone, fenchocamphorone, etc., can be indirectly methylated either by reduction of their hydroxymethylene compounds or by methylation of the oxalic ester condensation products.



Sabina ketone was converted by Claisen's method into *hydroxymethylene sabinaketone* (annexed formula), a white, crystalline substance, m. p. 51—52°. This on reduction with hydrogen in presence of palladium chloride gave *methylsabina ketone*, $C_{10}H_{16}O$, a heavy, high-refracting liquid, volatile in steam, and boiling at 221°.

Nopinone in the same way gave *hydroxymethylenenopinone* (annexed formula), m. p. 71—72°, which on reduction with hydrogen was converted into *methylnopinone*, $C_{10}H_{16}O$, a liquid, b. p. 215—216°, and yielding a *semicarbazone*, m. p. 179—180°.



Nopinone condenses with oxalic ester in presence of sodium ethoxide to give *nopinone oxalic* ester, $C_{13}H_{18}O_4$, a yellow oil, b. p. 158—160°/17 mm. It gives a red coloration with ferric chloride. By heating for several days, it is converted into *nopinonecarboxylic* ester, $C_{12}H_{18}O_3$, b. p. 230°, and giving a violet coloration with ferric chloride. The sodium salt of nopinone oxalic ester after heating for several days with excess of methyl iodide and alcohol gave, after hydrolysis, a small quantity of methylnopinone, together with a large excess of unchanged nopinone. G. F. M.

Mono- and Sesqui-terpene Series. Ernst Deussen (*J. pr. Chem.*, 1914, [ii], **90**, 318—335).—1. *Monoterpene Series* [with Max Ziem].—d-*Carvone hydrosulphide*, $(C_{10}H_{14}O_2)_2H_2S$, was prepared from

d-carvone, and crystallised from chloroform and ethyl acetate. It then had a constant m. p., 210—211°, and the irregularities previously observed are attributed to impurities. A 0·6026% solution in chloroform gave $[\alpha]^{18}$ + 48·71°. In benzene the compound is bimolecular, in acetic acid unimolecular. l-*Carvone hydrosulphide* was obtained of the same melting point, and a 0·6240% solution in chloroform gave $[\alpha]^{22} = -48·44°$. By mixing equal parts of the *d*- and *l*-compounds, the inactive substance was obtained. It formed silky needles, m. p. 189—190°.

Carvoxime tribromide was obtained by adding the theoretical quantity of bromine to carvoxime in chloroform solution in the cold. The *d*- and *l*-isomerides formed tabular crystals, m. p. 119—120° (decomp.), and $[\alpha]_D^{19}$ −15·17° (in 6·79% benzene solution) and + 14·87° (in 6·62% benzene solution) respectively. The racemic compound formed needles, m. p. 128° (decomp.). d- and l-*Carvoxime tetrabromide*, prepared in a similar manner to the above and crystallised from light petroleum, formed rhombic plates, m. p. 126—127°; the racemic compound melted at 121·5°. The rotations of *d*- and *l*-carvoxime tetrabromide was in the reverse direction to those of the oximes, $[\alpha]_D^{22}$ −10·70° and +11·09° in 7·44 and 8·35% benzene solution respectively. *Benzoylcarvoxime di-* and *tetra-bromides* were prepared by brominating in acetic acid. The *d*- and *l*-dibromides melt at 140—141°, the racemic dibromide at 121°; $[\alpha]_D^{20}$ +5·66° (for *d*-isomeride in 1·99% benzene solution), and $[\alpha]_D^{24}$ −5·11° (for *l*-isomeride in 2·21% solution). *d*- and *l*-Benzoylcarvoxime tetrabromides-*a* have m. p. 136—137°, and $[\alpha]_D$ +24·06° in the opposite sense to the original benzoylcarvoximes. *d*- and *l*-Benzoylcarvoxime tetrabromides-*b* melt at 119—120°, and have $[\alpha]_D$ +67·32°, also in the opposite sense. The racemic mixtures melt at 145° and 127° respectively.

2. *Sesquiterpene series* [variously with Carl Vielitz and Kurt Meyer].—*γ-Caryophyllene*, previously called *iso*caryophyllene (A., 1912, i, 368), was obtained by heating an alcoholic solution of *β*-caryophyllene nitrosite. It is regarded as an individual substance, and was subjected to reduction with hydrogen in presence of palladium in the same way that the mixture of *α*- and *β*-caryophyllene had previously been treated (*loc. cit.*). The *γ-dihydrocaryophyllene*, $C_{15}H_{26}$, thus obtained had the following physical constants: b. p. 124—124·5°, D^{21} 0·8872, α_D −29·41°, n_D^{21} 1·4880, M.R. 67·10 showing an exaltation of 0·5.

Although by reduction with hydrogen only one of the two double bonds of *β*-caryophyllene was reduced (*loc. cit.*) in the halogen derivatives of *β*-caryophyllene nitrosite, fully saturated compounds are represented. *β-Hydrochlorocaryophyllene nitrosite* is a blue compound, m. p. 140°, $[\alpha]_D$ +947·06° in 0·50433% solution in benzene. *β-Bromocaryophyllene nitrosite*, $C_{15}H_{24}O_3N_2$,HBr, prepared by bromination in chloroform, forms orange-yellow crystals, m. p. 104—105°. *β-Iodocaryophyllene nitrosite*, $C_{15}H_{25}O_3N_2I$, prepared by direct iodation, forms red crystals, m. p. 125°.

The substance, m. p. 116°, obtained by the action of sodium methoxide on *α*-caryophyllene nitrosochloride is now shown to be

nitroso-α-methoxycaryophyllene, $NO\cdot C_{15}H_{24}\cdot OMe$, and not $C_{15}H_{25}O_2N$ as previously stated (A., 1909, i, 814). Other sodium alkyloxides act in the normal way with production of α-nitrosocaryophyllene.

By the action of sulphuric acid on an acetic acid solution of caryophyllene, the formation of two new sesquiterpenes was observed, of which the physical constants were determined.

From β-caryophyllene nitrosite a number of alkyloxy-derivatives were prepared by the action of potassium hydroxide dissolved in the respective alcohol. *β-Nitrosomethoxycaryophyllene* formed coarse needles, m. p. 152°, $[\alpha]_D + 197{\cdot}25°$; *β-nitrosoethoxycaryophyllene*, m. p. 163°, $[\alpha]_D + 209{\cdot}2°$; *β-nitrosopropoxycaryophyllene*, silky needles, m. p. 134—135°, $[\alpha]_D + 191{\cdot}4°$; *β-nitrosoisoamyloxycaryophyllene*, aigrettes, m. p. 149·5—150·5°, $[\alpha]_D + 90{\cdot}73°$; *β-nitrosomonoethanoloxycaryophyllene*, quadratic tablets, m. p. 132—133°, $[\alpha]_D + 88{\cdot}97°$, and *β-nitrosobenzyloxycaryophyllene*, prisms, m. p. 188·5—189·5°, $[\alpha]_D + 188{\cdot}16°$. All these substances are insoluble in potassium hydroxide and hydrochloric acid, and absorb bromine.

From the mother liquors obtained in the preparation of β-caryophyllene nitrosite, a crystalline *compound*, $C_{13}H_{23}ON$, has been isolated.

Further experiments on the mixed melting point of α-caryophyllene nitrosobromide and α-bromocaryophyllene nitrosochloride confirm the fact that no lowering occurs, although the two substances have the same melting point and are certainly not identical. G. F. M.

The Constituents of Ethereal Oils. The Constituents of Costus Root Oil. F. W. Semmler and J. Feldstein (*Ber.*, 1914, **47**, 2687—2694. Compare *ibid.*, 2433).—The separation of costus root oil into eight fractions by distillation under reduced pressure has already been described, as has also the presence of an acid, $C_{15}H_{22}O_2$ (costic acid), and of two lactones, $C_{15}H_{20}O_2$ (costolactone) and $C_{15}H_{22}O_2$ (dihydrocostolactone), in the seventh and eighth fractions. The remaining fractions have now been examined.

Fraction 6, b. p. 175—190°/11 mm., after being freed from its acidic and lactonic constituents by means of alcoholic potassium hydroxide, yielded a considerable quantity of a sesquiterpene alcohol, $C_{15}H_{24}O$, to which the name *costol* is given; this substance was purified by conversion into the *hydrogen phthalate*, by hydrolysis of which it was obtained with the physical constants, b. p. 169—171°/11 mm., D^{21} 0·9830, n_D 1·52000, $\alpha_D + 13°$; the *acetate* was also prepared and had b. p. 174—177°/11 mm., D^{21} 0·9889, n_D 1·50152, $\alpha_D + 19°$. Costol is a diolefinic, bicyclic sesquiterpene alcohol oxidisable by an acetic acid solution of chromic acid to an *aldehyde*, $C_{15}H_{22}O$, which gives a characteristic *semicarbazone*, m. p. 217—218°; the aldehyde was recovered in a purer form from the semicarbazone and was found not to correspond with costol, but to be triolefinic; its physical constants were b. p. 164—165°/15 mm., D^{22} 0·9541, n_D 1·50645, $\alpha_D + 24°$. By treatment with phosphorus pentachloride, costol was converted into *costyl chloride*, $C_{15}H_{23}Cl$, b. p. 160—165°/13 mm., D^{22} 1·0005, n_D 1·52050, $\alpha_D + 32°$, which was reducible by sodium and alcohol to a diolefinic bicyclic sesquiterpene, *isocostene*, b. p. 130—135°/12 mm., D^{21} 0·9062,

n_D 1·50246, α_D + 31°; this hydrocarbon gives a liquid *hydrochloride*, which on elimination of hydrogen chloride regenerates the parent hydrocarbon.

That costol is the primary alcohol corresponding with costic acid is demonstrated by its artificial production on the reduction of the *methyl* ester of the latter substance with sodium and alcohol.

The fourth and fifth fractions contained, in addition to costol, a hydrocarbon, $C_{17}H_{28}$, to which the name *aplotaxene* is applied; this substance could not be obtained free from costol, but its physical constants approximately are b. p. 153—155°/11 mm., D^{21} 0·831, n_D 1·483, α_D 0°. From its low density the conclusion may be drawn that aplotaxene is an open-chain compound and its easy reduction by sodium and alcohol with formation of a *dihydroaplotaxene*, $C_{17}H_{30}$, b. p. 154—157°/11 mm., D^{21} 0·8177, n_D 1·47105, α_D 0°, indicates further that two of its ethylenic linkings are conjugated. Complete reduction by hydrogen and platinum black converted aplotaxene into an octahydro-derivative which proves to be identical with *n*-heptadecane; aplotaxene is therefore a tetraolefinic normal chain hydrocarbon.

In the second and third fractions, b. p. 100—130°/11 mm. and 130—150°/11 mm. respectively, the presence of two sesquiterpenes was discovered; *α-costene*, b. p. 122—126°/12 mm., D^{21} 0·9014, n_D 1·49807, α_D − 12°, forms a liquid *hydrochloride*, from which the original sesquiterpene can be regenerated, and appears to contain one of its two double linkings in a side-chain, for hydration produces an *alcohol*, $C_{15}H_{26}O$, b. p. 150—165°/14·5 mm., D^{21} 0·9491, n_D 1·50008, α_D + 20°. *β-Costene* is a triolefinic monocyclic sesquiterpene, b. p. 144—149°/19 mm., D^{22} 0·8728, n_D 1·4905, α_D + 6°.

Examination of the first fraction, b. p. 60—100°/11 mm., from the distillation of costus root oil showed the presence of phellandrene and camphene, together with a small quantity of an *alcohol*, $C_{10}H_{16}O$, b. p. 100—115°/14 mm.

Costus root oil has the composition: Camphene, 0·4%; phellandrene, 0·4%; terpene alcohol, 0·2%; α-costene, 6%, β-costene, 6%; aplotaxene, 20%; costol, 7%; dihydrocostolactone, 15%; costolactone, 11%; costic acid, 14%; resins, etc., 20%. D. F. T.

Oil of Eucalyptus globulus. Charles E. Burke and Charles C. Scalione (*J. Ind. Eng. Chem.*, 1915, **7**, 206—209).—Leaves of *Eucalyptus globulus* (Blue gum), grown in California, yielded 0·8% of oil having D^{20} 0·9052, $[\alpha]_D^{20}$ + 14·42°, n_D^{20} 1·46053, free acid 0·73, saponification number 2·5, acetyl number 56·0. The oil contains the following constituents: Aldehydes (butaldehyde, *iso*valeraldehyde, and hexaldehyde), 6%; pinene, 21 to 22%; cineol (eucalyptol), 47%; alcohols (eudesmol, globuol, with traces of free acids and esters), 23%. The chief difference between this oil and Australian eucalyptus oil lies in the high pinene content of the former, and to this fact is attributed the reason why the oil does not comply with the requirements of the U.S. pharmacopœia. The oil is insoluble in 70% alcohol. W. P. S.

Volatile Oil from Tubers of Kaempferia Ethelæ. Ernest Goulding and Oswald Digby Roberts (T., 1915, **107**, 314—319).—A small sample of a mixture of the tubers and rootlets of *Kaempferia*

Ethelae, when distilled in a current of steam, yielded a volatile oil to the amount of 1·9% of the dried material. The oil was pale yellow, mobile, and had a pleasant odour, resembling that of orange-flower oil, combined with a less agreeable odour, recalling that of crushed ivy leaves; it had D_{15}^{15} 0·936 and $[\alpha]_D + 30\,4°$. A larger quantity of the tubers examined subsequently yielded 2% of the volatile oil (calculated on the dried material); this was collected in two portions, a light oil and a heavy oil, constituting 93% and 7% of the total distillate respectively.

The light oil had D_{15}^{15} 0·9437, $\alpha_D^{22} + 19°47'$ (in 100 mm. tube), acid value 2·3, ester value 5·0, and ester value after acetylation, 47·6. The heavy oil was a dark brown, viscous liquid which gradually became semi-solid owing to the separation of a crystalline ketonic compound, further quantities of which were obtained from the higher boiling fractions of the light oil.

The *ketone*, $C_{24}H_{28}O_4$, m. p. 102°, $[\alpha]_D^{22} + 198°20'$ in solution in chloroform, forms large, transparent, diamond-shaped crystals which are colourless at first but gradually become brown. The crystals are almost inodorous, but in dilute alcoholic solution the compound exhibits a peculiar, characteristic odour, somewhat resembling that of crushed ivy leaves. It is highly unsaturated and readily combines with about twice its weight of bromine. It does not unite with sodium sulphite or with sodium hydrogen sulphite. On treatment with hydroxylamine, it yields a *hydroxylamine-oxime*, m. p. 184°, which forms hard, white crystals, and when shaken with dilute hydrochloric acid is converted into the *oxime*, $C_{24}H_{28}O_3{:}NOH$, m. p. 166°, which separates from solvents in white, crystalline tufts. The ketone furnishes a *benzoyl* derivative, m. p. above 260° (decomp.). On heating the ketone with *N*/2-alcoholic potassium hydroxide, it is converted into an amorphous *substance*, m. p. 200°.

The oil of *Kaempferia Ethelae* has approximately the following percentage composition: terpenes, including dipentene and probably pinene, 21·8; cineole, 17·2; ketonic compound, m. p. 102°, 13·0; alcohols, including linalool, 11·2; esters, chiefly or entirely methyl methylanthranilate, 1·3; phenols, 0·5; acids, chiefly or entirely acetic acid, 0·1; residue, probably chiefly sesquiterpenes, 34·9.

E. G.

Constitution of Caoutchouc and Allied Compounds. C. HARRIES (*Annalen*, 1914, **406**, 173—226).—For the reasons stated below, the author withdraws his *cyclo*octadiene formula for natural caoutchouc (A., 1905, i, 364) and replaces it by a cyclic structure in which the group $\cdot CH_2\cdot CH{:}CMe\cdot CH_2\cdot$ recurs many times; for the present the author is of opinion that the annexed formula is the most satisfactory representation of the natural caoutchouc molecule.

$$CH_2\begin{matrix}\diagup\\\diagdown\end{matrix}\begin{matrix}CH_2\cdot CMe{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CH\cdot CH_2\cdot CH_2\\ CH{:}CMe\cdot CH_2\cdot CH_2\cdot CH{:}CMe\cdot CH_2\cdot CH_2\cdot CH\end{matrix}\begin{matrix}\diagup\\\diagdown\end{matrix}CMe.$$

By the addition and the subsequent elimination of hydrogen chloride the double linkings may acquire new positions, the various *regenerates* mentioned below being thus formed.

In connexion with the new formula of natural caoutchouc, it is noteworthy that the ozonide of "sodium" isoprene caoutchouc, although exhibiting in freezing acetic acid a molecular weight corresponding with the formula $C_{10}H_{16}O_6$, yields amongst its products of decomposition acids of the formula $C_{16}H_{28}O_{10}$ and $C_{22}H_{36}O_{10}$, and consequently must have a molecular formula at least $C_{25}H_{40}O_{15}$.

[With EWALD FONROBERT.]—Para caoutchouc is converted into its hydrochloride and the latter is heated with anhydrous pyridine at 125—145°. The regenerate I. thus obtained has the same composition as, but is not identical with, the original caoutchouc. By ozonisation in ethyl acetate solution, it yields an ozonide, by the decomposition of which by water at about 125° the following substances are produced, the percentage being given in brackets: oxygen (0·068), hydrogen (0·044), carbon monoxide (0·183), carbon dioxide (0·845), hydrogen peroxide (1·04), lævulaldehyde (about 9·00), *n*-heptane-$\beta\zeta$-dione (8·7), undecanetrione (0·9), pentadecanetetraone (0·06), unidentified ketonic fraction (8·29), resinous ketonic fraction (9·3), formic acid (about 18·3), lævulic acid (about 12), succinic acid (1·5) [not formed in every case], hydrochelidonic acid (1·7), methyl*cyclo*hexenoneacetic acid (1·7), unidentified acid fraction (20), resinous acid fraction (6·4), resin from the ozonide (31·00).

The *undecanetrione* (probably the $\beta\zeta\kappa$-trione), $C_{11}H_{18}O_3$, colourless leaflets, m. p. 93—94°, is soluble in boiling water, forms a *trioxime*, needles, m. p. 123—124°, and *trisemicarbazone*, m. p. 205—206° (not quite pure), and by treatment with alcoholic sodium ethoxide undergoes intramolecular condensation, yielding a *monoketone*, possibly

$$\begin{matrix} CH_2\cdot CMe{:}C\cdot CH_2\cdot CH_2 \\ | \qquad\qquad\qquad\quad | \\ CH_2\cdot CH_2\text{–}C{:}CH\text{–}CO \end{matrix},$$

b. p. 130—140°/0·6 mm. (*semicarbazone*, $C_{11}H_{17}ON_3$, m. p. 210°). The *pentadecanetetraone* (probably the $\beta\zeta\kappa\xi$-tetraone), $C_{15}H_{24}O_4$, colourless leaflets, m. p. 123°, forms a crystalline *tetraoxime*, m. p. 112—113° (decomp.). The *methyl*cyclo*hexenoneacetic acid* (probably 1-*methyl*cyclo*hexen*-3-*one*-2-*acetic acid*) has been isolated in the form of the *phenylhydrazone*, colourless needles, m. p. 184—185°, of the methyl ester; the corresponding *semicarbazone* has m. p. 182°.

The production of the heptanedione by the decomposition of the ozonide is well in harmony with the *cyclo*octadiene formula of caoutchouc, but not so that of the triketone and the tetraketone; these must be scission products of a larger ring. Moreover, since the heptanedione and the undecanetrione appear to be produced always in a definite ratio, both substances are probably generated by the oxidation of one and the same cyclic structure. Regarding the size of this structure, the author calls attention, but does not attach undue importance, to the fact that the molecular weight in benzene of caoutchouc ozonide is 535 ($C_{25}H_{40}O_{15}$ requires 580). Being guided by this, and assigning to the natural caoutchouc molecule a C_{20}-ring, the necessity of a formula containing a repetition of the isoprene skeleton leads to the constitution given above for natural caoutchouc. Of course, the ozonide corresponding with this will yield only lævulaldehyde and lævulic acid by its decomposition, but when the caoutchouc

is converted through its hydrochloride into the regenerate I. a redistribution of the double linkings may occur; the author shows that by a shifting of two or more of the double linkings of the preceding formula of caoutchouc, the formation of the di-, tri-, and tetra-ketones, and of hydrochelidonic acid is readily explicable. Regenerate I. can be converted through its hydrochloride into regenerate II.; the ozonide of the latter yields by decomposition with water a very much larger proportion of products of high b. p. (compare Lichtenberg, following abstract) than does the ozonide of regenerate I. Consequently, in regenerate II., a renewed shifting of the double linkings must have occurred.

A second phenomenon which is unfavourable to the C_8-ring formula of caoutchouc is the thermal dissociation of caoutchouc hydrochloride. When this compound is heated at 100° in a vacuum, it loses hydrogen chloride until the percentage of chlorine has fallen to a value which remains constant at about 12·3. This value is of the same order of magnitude as that required if caoutchouc hydrochloride

$$(C_{20}H_{32},4HCl\,;\ C_{25}H_{40},5HCl\,;\ C_{30}H_{48},6HCl\,?)$$

lost all but one of its mol. of hydrogen chloride. C. S.

Transformation Products of Caoutchouc Hydrogen Haloids and Their Thermal Dissociation. Otto Lichtenberg (*Annalen*, 1914, **406**, 227—239. Compare preceding abstract).—The regenerate I. obtained from gutta-percha is not only very similar in external appearance to regenerate I. from caoutchouc, as stated by Harries and Fonrobert, but its ozonide by decomposition with water yields formic acid, lævulic acid and its aldehyde, and *n*-heptane-$\beta\zeta$-dione in proportions quite similar to those obtained in the case of the ozonide of regenerate I. of caoutchouc. Whether the triketone and the tetraketone are also formed unfortunately could not be ascertained owing to lack of sufficient gutta-percha regenerate.

Caoutchouc-regenerate I. forms a *hydrochloride*, $C_{10}H_{16},2HCl$, pale brown mass, decomp. 145—185°, a *bromide*, $C_{25}H_{40}Br_8$, colourless powder, decomp. 80—145°, and a *nitrosite*, $C_{10}H_{15}O_7N_3$, yellow powder.

Regenerate Ia, obtained by heating with pyridine the partly dechlorinated caoutchouc hydrochloride (preceding abstract), is pale brown, transparent, and very elastic; its *hydrochloride* and *nitrosite* are described.

Caoutchouc-regenerate II., obtained from regenerate I. through its hydrochloride, is an elastic, violet-black substance, which is distinctly more soluble than caoutchouc in benzene and forms a *hydrochloride*, brown powder, decomp. 135—185°, *bromide*, brownish-white substance, decomp. 115—145°, *nitrosite*, yellow powder, decomp. 130—135°, and *ozonide*, golden-yellow, viscous oil. The decomposition of the last compound by water yields formic and lævulic acids, lævulaldehyde, and *n*-heptane-$\beta\zeta$-dione, together with a large quantity of unidentified substances of high b. p.

The thermal dissociation of caoutchouc hydrochloride has been mentioned (preceding abstract); that of the hydrobromide is similar but more rapid.

By prolonged boiling in toluene or xylene, caoutchouc undergoes a change of some sort, but still forms a hydrochloride. C. S.

The Swelling of Caoutchouc in Organic Liquids. D. Spence and G. D. Kratz (*Kolloid. Zeitsch.*, 1914, **15**, 217—226).—The examination of the swelling properties of different varieties of caoutchouc in contact with organic liquids has shown that the capacity to swell is not common to all kinds of caoutchouc, but is limited to the raw material. Para caoutchouc, which has been washed, dried and rolled, is no longer capable of swelling, and this change in properties appears to be brought about even when the rolling has been continued for a very short period. Different samples of raw Para caoutchouc also exhibit considerable variations in swelling power, and it would seem, therefore, that the previous history and the foreign substances present play an important part in connexion with this phenomenon.

The swelling of Para caoutchouc has been investigated in a number of liquids, the method employed consisting in immersing circular discs of the caoutchouc in the liquids and from time to time measuring the change in dimensions of the discs and also the increase in weight. If the liquids are arranged in decreasing order according to the volume of liquid which is absorbed by one gram of caoutchouc when the maximum swelling has been attained, the following series is obtained: (1) carbon tetrachloride and chloroform, (2) carbon disulphide, (3) benzene, toluene and xylene, (4) ethyl ether. Trichloroacetic acid in less than 1% concentration and acetic acid in less than 10% have no appreciable influence on the maximum swelling or on the velocity of the process. At higher concentrations, trichloroacetic acid increases both the maximum swelling and the velocity, and this effect increases with increasing concentration of the acid. H. M. D.

The Regeneration of Caoutchouc from its Tetrabromide. F. Kirchhof (*Kolloid. Zeitsch.*, 1914, **15**, 126—131).—The experiments described were undertaken with the object of throwing further light on the nature of the process by which bromine is removed from caoutchouc tetrabromide and on the conditions under which caoutchouc is regenerated (compare Ostromisslensky, A., 1912, i, 280, 284). By the action of alcoholic potash at 100°, half the bromine is removed with the formation of a dibromide. This substance is a yellow powder which swells considerably in contact with carbon disulphide, but does not dissolve in this liquid. It is insoluble in acetone, alcohol and ethyl ether, and unlike the tetrabromide it does not give Weber's reaction.

The removal of further bromine requires the application of a higher temperature, but by heating with metallic calcium and alcohol at 170—180° or with aniline at 180—190°, the greater part of the remaining bromine can be removed.

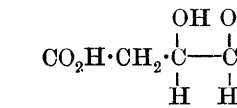
Experiments made to regenerate caoutchouc from the tetrabromide have shown that metallic calcium yields a non-elastic form which is considered to be isomeric with normal caoutchouc. Regeneration by heating with aniline gives an elastic modification which closely resembles the original caoutchouc from which the tetrabromide was prepared. H. M. D.

Anhydrogitalin and a By-product of the Manufacture of Digitoxin. H. KILIANI (*Ber.*, 1915, **48**, 334—349).—According to Kraft (A., 1912, i, 373) aqueous extracts of digitalis contain an active glucoside, gitalin, which very readily loses water and yields anhydrogitalin. The author has previously shown (A., 1914, i, 309, 857) that gitalin is a mixture containing pre-formed anhydrogitalin. In the present communication, further experiments with the latter substance are described, the name being retained, although its significance has been lost. In the hope of isolating a second form of digitoxin, the by-products obtained during the manufacture of the commercial article have been investigated.

Anhydrogitalin is prepared by the addition of ether to a solution of gitalin in methyl alcohol and chloroform (equal volumes). It has m. p. 255°, after sintering at 250°. Analyses agree with the formula $C_{33}H_{52}O_{12}$ instead of $C_{28}H_{46}O_9$, given by Kraft. Hydrolysis with acid (100 c.c. 50% alcohol + 1 c.c. concentrated hydrochloric acid) yields anhydrogitaligenin, m. p. 200° (216—219° according to Kraft), and digitoxose, m. p. 101°. The formula of anhydrogitaligenin appears to be $C_{21}H_{30}O_5$, and hydrolysis of the glucoside thus occurs in accordance with the scheme: $C_{33}H_{52}O_{12} + H_2O = C_{21}H_{30}O_5 + 2C_6H_{12}O_4$.

The sparingly soluble by-products of the manufacture of digitoxin were contaminated with some coloured impurity which could not be removed in a practical manner. The mass was therefore extracted with methyl alcohol, and, without further purification, hydrolysed in the same manner as anhydrogitalin. Digitoxose, m. p. 101°, $[\alpha]_D + 45{\cdot}6°$, was thereby obtained (identified also by conversion into digitoxonic acid, its phenylhydrazide and brucine salt), and a substance, $C_{22}H_{32}O_6$, shining leaflets, m. p. 205—206°. The latter is dissolved by sodium hydroxide, yielding a *sodium* salt from which hydrochloric acid regenerates an isomeric *compound*, $C_{22}H_{32}O_6$. The sodium salt is readily attacked by permanganate; the corresponding *barium*, *calcium*, *magnesium*, *zinc* and *copper* salts have been investigated. With benzoyl chloride in pyridine solution, a *dibenzoyl* derivative, $C_{22}H_{30}O_6Bz_2$, which shrinks at 190° but has no distinct m. p., is produced.

Oxidation of digitoxose with nitric acid (D 1·2) under definite conditions and treatment of the product with calcium carbonate yields calcium *i*-tartrate, calcium digitoxonate, and calcium dihydroxyglutarate. The identity of the former is confirmed by isolation of the free acid and of the zinc and copper salts. The crude dihydroxyglutaric acid obtained from the calcium salt was purified by means of the quinine salt, $C_5H_8O_6,2C_{20}H_{24}O_2N_2,5H_2O$, and converted into the barium salt, which had $[\alpha]_D + 4{\cdot}8°$ when dissolved in the requisite quantity of dilute hydrochloric acid. The isolation of *i*-tartaric acid points to the fact that the dihydroxyglutaric acid from digitoxose must be one of the two meso-forms (annexed formula).



Finally, attempts have been made to ascertain the formula of the parent glucoside which forms the chief constituent of the sparingly soluble by-product. This has been obtained as a perfectly white precipitate, m. p. 190°, by treatment with methyl alcohol–

chloroform–ether, analyses of which agree only approximately with the formula $C_{34}H_{52}O_{12}$; there is no proof of the uniformity of the fraction. H. W.

Anthocyanins. II. Colouring Matter of the Rose. RICHARD WILLSTÄTTER and THOMAS J. NOLAN (*Annalen*, 1915, **408**, 1—14. Compare A., 1914, i, 564; Willstätter and Everest, A., 1913, i, 1371; Everest, A., 1914, i, 978; this vol., i, 25).—The dried powdered petals of *Rosa gallica* are digested with 2·5% methyl-alcoholic hydrogen chloride. After being kept overnight, the mixture is filtered and the filtrate is treated with ether. The resulting undried precipitate is digested with a mixture of methyl alcohol and glacial acetic acid, whereby the impurities are dissolved and the cyanin chloride remains as a microcrystalline residue. It is purified by solution in boiling water and precipitation with 3% ethyl-alcoholic hydrogen chloride. The chloride is thus obtained in metallic, microcrystalline rhombs, $C_{27}H_{31}O_{16}Cl,2\frac{1}{2}H_2O$. The amount of the water of crystallisation depends on the conditions under which the chloride (from the rose and also from the cornflower) has been crystallised.

The identity of the anthocyanin in the rose with that in the cornflower has been proved by the identities of the specific rotation, absorption spectra, and solubility in dilute hydrochloric acid and in ethyl alcohol of the cyanin chlorides, and by quantitative hydrolysis to cyanidin and dextrose (2 mol.).

Cyanidin chloride has the formula $C_{15}H_{11}O_6Cl$, not $C_{16}H_{13}O_7Cl$ (Willstätter and Everest, *loc. cit.*). It retains $1H_2O$ with great tenacity, and is converted by hot aqueous alcohol into the ψ-base, $C_{15}H_{12}O_7,H_2O$, colourless crystals, which changes to the isomeric, dark violet colour-base at 130°. C. S.

Anthocyanins. III. Colouring Matter of the Whortleberry. RICHARD WILLSTÄTTER and HEINRICH MALLISON (*Annalen*, 1915, **408**, 15—41).—The skins of the whortleberry (*Vaccinium vitis idaea*) are digested with glacial acetic acid for eight days, and the extract is shaken with ether ($2\frac{1}{2}$ vol.). The dark red, viscous precipitate undergoes further treatment with glacial acetic acid, the resulting solution being finally fractionally precipitated with ether. The second fraction, which contains most of the colouring matter, is dissolved in water, and picric acid is added. The precipitate of potassium picrate and the picrate of the colouring matter is extracted with methyl alcohol, which dissolves the latter, and the alcoholic solution is treated with ether. The precipitated picrate is finally crystallised from water.

The colouring matter of the whortleberry is called *idaein*; it is nearly allied to cyanin, and by hydrolysis yields galactose (1 mol.) and cyanidin, the latter being identical with the cyanidin obtained from cyanin of the rose and of the cornflower.

The preceding method of isolating the colouring matter in the form of its picrate has been successfully applied in other cases (compare Willstätter and Zollinger, following abstract).

Idaein picrate is obtained as a brownish-red powder consisting of

crimson-red, microscopic needles. Its dilute aqueous or alcoholic solution changes in colour from orange-red to pale yellow owing to the conversion, despite the presence of the picric acid, of the idaein into the isomeric ψ-base; the original colour is restored by the addition of hydrochloric acid.

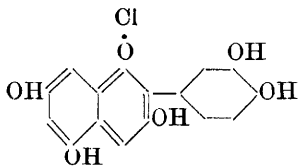
By treatment with methyl-alcoholic hydrogen chloride and subsequently with ether, the picrate is converted into *idaein chloride*,

$$C_{21}H_{21}O_{11}Cl,2\tfrac{1}{2}H_2O,$$

m. p. 210° (decomp.), microscopic, greyish-violet or brownish-red, monoclinic prisms with a green, metallic reflex. Idaein chloride is lævorotatory, $[\alpha]_C - 219° \pm 15°$ in 0·5% hydrochloric acid, and exhibits rotatory dispersion; its absorption spectrum is similar to, but quite distinct from, that of cyanin chloride.

Idaein differs from cyanin in its solubilities and in its behaviour with alkalis. It develops a violet coloration with sodium carbonate or hydrogen carbonate, and with alkali hydroxides a blue coloration which changes rapidly to green and yellow. It also differs from cyanin and other diglucosides in its behaviour in the partition test. When distributed between amyl alcohol and 7% sulphuric acid, idaein can be completely removed from either of the liquid phases by repeated washing with the other solvent. Idaein develops characteristic colour reactions with metallic salts and is converted into a colourless leuco-compound by reducing agents.

The revised formula of cyanidin (preceding abstract) leads to important consequences, since it brings pelargonidin, $C_{15}H_{10}O_5$, cyanidin, $C_{15}H_{10}O_6$, and delphinidin, $C_{15}H_{10}O_7$, into a natural family, the members of which differ from one another in the number of hydroxyl groups they contain and are isomeric with members of the flavone and of the flavonol series. In accordance with the latter relation it has been found that anthocyanidins yield a phenol and a carboxylic acid by fusion with potassium hydroxide, cyanidin, for example, yielding phloroglucinol and protocatechuic acid. The authors advance reasons for their opinion that cyanidin chloride has the annexed formula, and that pelargonidin chloride contains one OH less, in position 3′, and delphinidin chloride contains one OH more, in position 5′. C. S.



Anthocyanins. IV. Colouring Matter of the Scarlet Pelargonium. Richard Willstätter and Elmer K. Bolton (*Annalen*, 1915, **408**, 42—61).—The anthocyanin of the pelargonium has been examined by Griffiths in 1903 and by Grafe in 1911, but their observations are contradicted by the authors in almost every detail.

The flowers of the scarlet pelargonium (*Pelargonium zonale*, var. *meteor*) contain only one colouring matter, which is called *pelargonin*. Like cyanin, it forms crystalline oxonium salts (it occurs as such in the scarlet flowers), and is a diglucoside, yielding by hydrolysis with hydrochloric acid, dextrose (2 mol.) and pelargonidin.

Pelargonin can be isolated from the flowers by digesting them for a month with glacial acetic acid and treating the extract

with alcoholic hydrogen chloride and ether, but a more expeditious process, which yields a purer product, is the following. The fresh flowers, which contain as much as 0·66—0·7% of pelargonin, are digested for several days with 96% alcohol, and the extract, which lightens in colour owing to the transformation of the colouring matter into the ψ-base, is treated with an excess of 20% alcoholic hydrogen chloride and ether. The crimson-red precipitate is dissolved in boiling 2% methyl-alcoholic hydrogen chloride, and the filtered solution is treated with 10% hydrochloric acid, whereby the oxonium chloride is precipitated. *Pelargonin chloride*, $C_{27}H_{31}O_{15}Cl$, m. p. about 180° (decomp.), $[\alpha]_D^{19\cdot5}$ − 291° and $[\alpha]_{614}$ − 180° in 0·1% hydrochloric acid, crystallises from methyl-alcoholic hydrogen chloride in scarlet-red, elongated, slender needles containing $4H_2O$. Its cold, aqueous, orange-coloured solution undergoes hydrolysis, yielding a violet solution of the colour-base, which in its turn changes to the colourless ψ-base. The yellowish-red, methyl-alcoholic solution of the chloride is more stable and exhibits a distinct greenish-yellow fluorescence, which is characteristic of pelargonin. Pelargonin chloride does not develop a characteristic coloration with ferric chloride; with sodium carbonate, aqueous ammonia, or sodium hydroxide a violet solution is obtained, which changes through greenish-red to yellow. In alcoholic solution alkalis produce a blue coloration changing to violet by dilution with water. By boiling for a few minutes with alcohol, pelargonin chloride is converted into a *basic pelargonin chloride*, $2C_{27}H_{31}O_{15}Cl,C_{27}H_{30}O_{15}$, dark violet, metallic needles containing $12H_2O$.

Pelargonin, $C_{27}H_{30}O_{15}$, dark violet, amorphous powder, obtained by adding sodium acetate to a faintly acid solution of the chloride, crystallises from boiling 90% acetic acid in the form of the *basic acetate*, $2C_{27}H_{30}O_{15},C_{27}H_{31}O_{15}\cdot OAc$, pale red needles containing acetic acid, by the loss of which in a vacuum the colour changes to brownish-violet.

Pelargonidin chloride, $C_{15}H_{11}O_5Cl$ (for constitution see preceding abstract), m. p. above 350°, crystallises in stout plates or in reddish-brown prisms; by exposure to the air it absorbs $1H_2O$, and becomes red. It does not develop a characteristic reaction with ferric chloride, forms a blue solution with sodium carbonate, and is converted by hot water containing a trace of sodium hydrogen carbonate into the *ψ-base*, $C_{15}H_{12}O_6$, colourless prisms.

By heating with 60% potassium hydroxide at a temperature below 100°, pelargonidin chloride yields phloroglucinol; by fusion with potassium hydroxide at 220° the other anticipated fission product, *p*-hydroxybenzoic acid, has been obtained together with a small amount of protocatechuic acid. C. S.

Anthocyanins. V. Anthocyanin in the Larkspur. Richard Willstätter and Walter Mieg (*Annalen*, 1915, **408**, 61—82).—In the first paper the theory was advanced that the varied colours of many flowers are due to different forms of a single anthocyanin which acquires a red, violet, or blue colour, according as the cell-juice is acid, neutral, or alkaline. The theory has now been tested successfully in the case of the violet flowers of *Delphinium consolida*. These

contain an anthocyanin which is called *delphinin*. Unlike other anthocyanins which have been examined, delphinin forms stable solutions in neutral solvents, a colourless ψ-base not being produced. Moreover, since delphinin is insoluble in water and in concentrated alcohol, but dissolves in dilute alcohol, the authors have been able to isolate the colouring matter without employing chemical reagents and thus to prove that, in accordance with the theory, it occurs in the flowers in a neutral form unaccompanied by any mineral constituent; the violet colour is changed to blue by alkalis, even by sodium hydrogen carbonate, and is changed to red by acids, even by acetic acid.

The preceding method of isolating delphinin is exceedingly troublesome. Much more convenient is the usual process of isolating anthocyanins in the form of their oxonium chlorides. The dried flowers are powdered and extracted with aqueous alcoholic hydrochloric acid, the extract being treated with an equal volume of ether which precipitates delphinin chloride and many impurities as an oil. The latter are removed to a considerable extent by treatment with methyl and ethyl alcohols and ether. The crude product is heated on the water-bath with 2% hydrochloric acid, which does not attack the glucoside, but hydrolyses the colloidal impurities and thereby diminishes their solvent action on the delphinin chloride, so that the latter is precipitated in an amorphous condition by the addition of more concentrated hydrochloric acid. The chloride does not readily assume the crystalline condition, the amorphous substance requiring careful treatment with warm 3% hydrochloric acid in order that a portion of it may be obtained in the crystalline state.

Delphinin chloride, $C_{41}H_{39}O_{21}Cl,12H_2O$, crystallises in dark brownish-red, prismatic plates, which lose only $10H_2O$ even in a vacuum at 130° and then sinter at 150—160° and have m. p. 200—203° (decomp.). The chloride is immediately hydrolysed by water, and is insoluble in almost all of the usual organic solvents. It has $[\alpha]_0$ $-1364° \pm 150°$ and $[\alpha]_{614}$ $-2273° \pm 150°$ in 0·1% hydrochloric acid, and develops an intense blue coloration with ferric chloride in faintly acid solution, the colour being changed to violet by alcohol.

By rapid hydrolysis with hot, moderately concentrated hydrochloric acid, delphinin chloride is converted into dextrose (2 mol.), *p*-hydroxybenzoic acid (2 mol.), and *delphinidin chloride*, $C_{15}H_{11}O_7Cl$, brownish-black, metallic plates containing $2H_2O$ (for constitution see Willstätter and Mallison, preceding abstract). Delphinidin chloride is a quinonoid oxonium salt which forms blue salts with alkalis, very stable red salts with acids, and is converted in neutral solution into the *ψ-base*, $C_{15}H_{12}O_8$, colourless prisms containing $4H_2O$. Delphinidin chloride is decomposed by boiling 75% potassium hydroxide, yielding phloroglucinol, and by fusion with potassium hydroxide at 250°, yielding phloroglucinol, gallic acid and pyrogallol.

Other varieties of *Delphinium* contain an anthocyanin (probably another glucoside of delphinidin) which can be converted into a ψ-base in the usual manner. C. S.

Anthocyanins. VI. Colouring Matter of the Grape and of the Bilberry. Richard Willstätter and Ernst H. Zollinger (*Annalen*, 1915, **408**, 83—109).—The authors criticise the methods of,

and the results recorded by, previous investigators; attempts to isolate anthocyanins in the form of lead salts are bound to be unsuccessful because the precipitating action of lead acetate is too general to lead to even a partial separation of the anthocyanin from its accompanying impurities.

The fresh skins of the dark blue grapes (*Vitis vinifera*) of North Italy are digested with glacial acetic acid during at least a week, the filtered extract is treated with thrice its volume of ether, the dark red syrupy precipitate is dissolved in water, and the filtered solution is treated with an excess of cold aqueous picric acid, whereby the anthocyanin (which is called *oenin*) is precipitated in the form of the *picrate*, tufts of crimson-red needles. A methyl-alcoholic solution of the picrate is treated with 17% methyl-alcoholic hydrogen chloride, and then with ether and light petroleum, whereby the chloride is obtained in the amorphous state; it is crystallised from a mixture of methyl and ethyl alcohols and 10% hydrochloric acid.

Oenin chloride, $C_{23}H_{25}O_{12}Cl$, dark red or brownish-red prisms with a green lustre, containing varying amounts of water of crystallisation, is easily soluble in water. In consequence of hydrolytic dissociation, the brownish-red colour of the solution changes on dilution to violet, this in its turn disappearing as the colour-base changes to the colourless *ψ-base*; the last change is prevented even by 0·2% tartaric acid solution. Oenin is strongly lævorotatory; in 0·1% hydrochloric acid it has $[\alpha]_c - 421° \pm 30°$ and $[\alpha]_{627} - 542° \pm 60°$.

Oenin is a monoglucoside. By rapid hydrolysis with 25% hydrochloric acid it yields dextrose and *oenidin chloride*, $C_{17}H_{15}O_7Cl$, dark brown prisms and needles with a bronze lustre, containing $1\frac{1}{2}H_2O$. Oenidin chloride is rapidly converted into the colourless *ψ-base* in warm aqueous solution. It contains two methoxyl groups, and is converted into delphinidin by hydriodic acid and phenol or acetic anhydride. It is very easily decomposed by warm concentrated potassium hydroxide, yielding phloroglucinol; the decomposition by alkali at 220—240° produces phloroglucinol, and a mixture probably of gallic acid, its methyl ether, and pyrogallol.

The anthocyanin of the bilberry (*Vaccinium myrtillus*), which is called *myrtillin*, is isolated as follows: The skins of the fresh berries are dried, powdered, and boiled with methyl or ethyl alcohol containing a few drops of alcoholic hydrogen chloride. The cold extract is treated with 2% alcoholic hydrogen chloride, ether is added (preferably preceded by glacial acetic acid), and the syrupy precipitate is purified either by converting the myrtillin into its *picrate*, red needles, or better, although the loss of material is greater, by treating its filtered aqueous solution with concentrated hydrochloric acid at 0°, whereby the chloride is obtained in the amorphous state; it is then obtained crystalline by the addition of ether to its solution in 2% methyl-alcoholic hydrogen chloride.

Myrtillin chloride, $C_{22}H_{23}O_{12}Cl$, bronze-brown crystals with a copper lustre, containing $4H_2O$, is very nearly allied to oenin chloride. It yields by hydrolysis a sugar (the identification and estimation of which have not yet been attempted owing to lack of material) and *myrtillidin chloride*, $C_{16}H_{13}O_7Cl$, dark brown prisms with a green

lustre. Myrtillidin chloride is nearly allied to oenidin chloride. The two anthocyanidins, however, and also the two parent anthocyanins are readily differentiated by their behaviour with alcoholic ferric chloride; whilst oenin and oenidin develop only a reddish-violet coloration, myrtillin and myrtillidin produce intensely blue solutions, the colour of which is changed to violet by dilution.

Myrtillidin chloride contains only one methoxyl group and yields delphinidin in the Zeisel reaction. It is decomposed by potassium hydroxide and yields gallic acid and phloroglucinol. The preceding facts, taken in conjunction with the colour reactions with ferric chloride, lead the authors to the opinion that myrtillidin chloride and oenidin chloride are respectively the 7-monomethyl and the 3 : 4′-dimethyl ethers of delphinidin chloride (compare Willstätter and Mallison, preceding abstract) C. S.

Anthocyanins. VII. Colouring Matter of the Hollyhock. Richard Willstätter and Karl Martin (*Annalen*, 1915, **408**, 110—121).—*Althaein*, the anthocyanin of the hollyhock (*Althaea rosea*), is obtained by digesting the dried, powdered flowers with 2% methyl-alcoholic hydrogen chloride, and treating the extract with ether. The precipitate of very impure althaein chloride has been treated in several ways, all of which are admittedly provisional in character, since this paper is only a preliminary one.

Althaein chloride, $C_{22}H_{23}O_{12}Cl$, dark brown prisms with a bronze lustre, containing $4H_2O$, has $[\alpha]_{623} - 655°$, $[\alpha]_C - 545°$, and $[\alpha]_{692} - 291°$ in 0·1% hydrochloric acid, and is a monoglucoside according to the evidence at present available. It yields dextrose (?) and myrtillidin chloride by hydrolysis with boiling, moderately concentrated hydrochloric acid. C. S.

Anthocyanins. VIII. Colouring Matter of the Wild Mallow. Richard Willstätter and Walter Mieg (*Annalen*, 1915, **408**, 122—135).—*Malvin*, the anthocyanin in the violet flowers of the wild mallow (*Malva silvestris*), is very easily obtained by the picrate method. The dried powdered flowers are digested with 2% methyl-alcoholic hydrogen chloride and about 1/33 of the volume of concentrated hydrochloric acid. The purplish-red extract is treated with ether, the precipitate is digested with cold methyl alcohol, and the resulting solution is diluted with ethyl alcohol and with ether, whereby a purer product is obtained. This is agitated with 1% hydrochloric acid and warmed at 50° with 1·5% aqueous picric acid. *Malvin picrate* is thus obtained in brownish-red or cherry-red, slender needles with a metallic lustre. By solution in methyl alcohol, treatment with methyl-alcoholic hydrogen chloride, and precipitation with ether, the picrate is converted into the chloride, which is characterised by its sparing solubility and its tendency to crystallise.

Malvin chloride, $C_{29}H_{35}O_{17}Cl$, brownish-red, elongated prisms with an intense green lustre, containing $8H_2O$, does not develop a coloration with ferric chloride, yields a blue solution with sodium carbonate, and in dilute solution changes very rapidly to the colourless ψ-base. By

hydrolysis with boiling 20% hydrochloric acid it yields dextrose (2 mol.) and *malvidin chloride*, $C_{17}H_{15}O_7Cl$, dark brown crystals with a metallic bronze lustre, containing $2H_2O$. The latter substance is isomeric with oenidin chloride and is nearly related to it, differing from it only in the position of one methyl group. Malvidin chloride contains two methoxyl groups and yields delphinidin in the Zeisel reaction. It is very slightly soluble in dilute hydrochloric or sulphuric acid, does not develop a coloration with ferric chloride, and yields phloroglucinol, its methyl ether, and gallic acid and its methyl ether by decomposition with potassium hydroxide under different conditions.

A tabulated statement is given of the properties and the colour reactions of pelargonin, cyanin, delphinin, oenin, and malvin, and of the corresponding anthocyanidins. C. S.

Anthocyanins. IX. Colouring Matter of the Peony. Richard Willstätter and Thomas J. Nolan (*Annalen*, 1915, **408**, 136—146).—*Peonin*, the anthocyanin of the flowers of the peony, is present to the extent of about 3—3·5%, and about one-fifth of it can be isolated in the pure state. The dried, powdered flowers are digested for two hours with 2% methyl-alcoholic hydrogen chloride and the extract is treated with ether. The dark red, syrupy precipitate is agitated with warm, about 0·7% methyl-alcoholic hydrogen chloride and glacial acetic acid is then added, and the mixture is kept for sixty hours in order to effect the hydrolysis of the colloidal impurities which increase the solubility and diminish the tendency to crystallisation of the peonin chloride. The friable residue is collected, washed, dried, boiled several times with 2% methyl-alcoholic hydrogen chloride in small quantities, and finally crystallised from boiling *N*/2-hydrochloric acid.

Peonin chloride, $C_{28}H_{33}O_{16}Cl$, reddish-violet needles containing $5H_2O$, m. p. 165° (decomp.), is a diglucoside which is very nearly allied to cyanin chloride, the colour of the solution in 7% sulphuric acid, the velocity of the transformation into the colourless ψ-base, and the colour reactions with sodium hydroxide, carbonate, and acetate being the same for both anthocyanins. Peonin chloride, however, dissolves easily in cold water, forms a reddish-violet solution in ethyl alcohol, and scarcely changes its colour in the presence of ferric chloride. *Peonin picrate* crystallises in brownish-red needles. The rotation of peonin chloride can only be measured in white light; it has $[\alpha]^{27} - 191° \pm 5°$ in 0·05% hydrochloric acid.

By boiling for two and a-half minutes with 20% hydrochloric acid, peonin chloride is hydrolysed and yields dextrose (2 mol.) and *peonidin chloride*, $C_{16}H_{13}O_6Cl$, reddish-brown needles containing $1H_2O$. The latter is a monomethyl ether of cyanidin, and is converted into this by heating with hydriodic acid. Naturally, it closely resembles cyanidin in most of its reactions, but differs from it in its greater solubility in water, in its colour reactions in alcoholic solution with potassium acetate, and in developing a violet-red coloration with alcoholic ferric chloride. *Peonidin picrate* crystallises in brownish-red needles.

A table is given comparing the properties and reactions of cyanin and peonin and of cyanidin and peonidin. C. S.

Anthocyanins. X. Variations in the Colours of Flowers. RICHARD WILLSTÄTTER and HEINRICH MALLISON (*Annalen*, 1915, **408**, 147—162).—The constitutions of cyanidin and of pelargonidin have recently been established. Willstätter and Mallison (A., 1914, i, 1081) have obtained cyanidin by the reduction of quercetin by magnesium in acid media, whilst Willstätter and Zechmeister (*Sitzungsber. K. Akad. Wiss., Berlin*, 1914, 886) have synthesised pelargonidin by demethylating the product obtained by the reaction of 3 : 5 : 7-trimethoxycoumarin and magnesium anisyl bromide.

The paper deals mainly with the natural and the chemical causes of the variability of the colours of flowers. Factors such as the content of colouring matter in the flower, the presence of yellow pigments, the acidity or alkalinity of the cell juices, etc., are of paramount importance. Some plants produce more than one anthocyanin; for example, the blue flowers of the cornflower contain cyanin, whilst the pink blooms, growing on the same plant, contain pelargonin. Similar results have been obtained with varieties of *Pelargonium* and of the dahlia. C. S.

A Lecture on Vegetable Colouring Matters. RICHARD WILLSTÄTTER (*Ber.*, 1914, **47**, 2831—2874. Compare A., 1913, i, 1371; 1914, i, 564, and preceding abstracts).—A résumé of the researches of the author and other investigators on chlorophyll and related substances. A. J. W.

Oxonium Compounds. AL. FAVORSKI and E. VENUS (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 133—141).—The *pinacone*,

$$OH\cdot CMe_2\cdot CPh(OH)\cdot C{:}CPh,$$

obtained by the interaction of magnesium phenylacetylene bromide and benzoyldimethylcarbinol, forms colourless, triclinic crystals, m. p. 93—93·5°, and exhibits the normal molecular weight in freezing benzene.

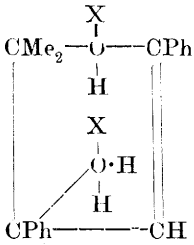
4-*Hydroxy*-2 : 4-*diphenyl*-5 : 5-*dimethyl*-4 : 5-*dihydrofuran*,

$$O<\begin{matrix}CPh=CH\\ |\\ CMe_2\cdot CPh\cdot OH\end{matrix}$$

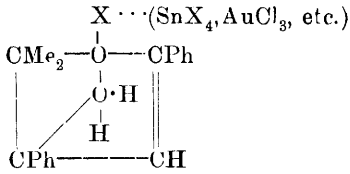
formed by boiling the pinacone with 20% sulphuric acid solution, has m. p. 101—102°, and exhibits normal cryoscopic behaviour in benzene. Its formation is analogous to the conversion observed by Palladin, but not yet published, of the glycol, $OH\cdot CHPh\cdot CPh(OH)\cdot C{:}CPh$, into 4-hydroxy-2 : 4 : 5-triphenyl-4 : 5-dihydrofuran; the latter, however, readily loses the elements of water, yielding 2 : 4 : 5-triphenylfuran. It exhibits distinct basic properties and forms salts with both mineral and organic acids; its solutions in aqueous mineral acids are yellowish-green, and with concentrated sulphuric acid it yields a blue, fluorescent solution. Its *hydrochloride*, $C_{18}H_{18}O_2,2HCl,2H_2O$, has m. p. 61—62° or 105—107° (anhydrous). Its *platinichloride*, *aurichloride*, *stannichloride*, m. p. 150—152°, *hydrobromide*, m. p. 157° or, in a sealed tube, 154°, *stannibromide*, m. p. 180—182° (decomp.), *hydriodide*, m. p. 174—176° in a closed capillary, *sulphate*, $C_{18}H_{18}O_2,2H_2SO_4$, m. p. 163° in a closed tube, and its *trichloroacetate*, $C_{18}H_{18}O_2,2CCl_3\cdot CO_2H$, m. p. 116—118° (decomp.), were prepared. Its *acetyl* derivative, $C_{18}H_{17}O_2Ac$,

m. p. 141—142°, is distinctly acidic in character, but exhibits marked stability towards alkalis.

All the anhydrous salts of this base contain 2 mols. of acid per 1 mol. of the furan derivative, but these 2 mols. of acid are not in similar condition, since only one of them enters into the constitution of the platinichloride, $(C_{18}H_{18}O_2)_2,H_2PtCl_6$, and analogous compounds. On the basis of the oxonium theory, both oxygen atoms must be regarded as oxonium in type, the structure of the salts being represented by formula I. Owing to the marked difference in stability between



(I.)



(II.)

oxonium salts of hydroxylic oxygen and those of ethereal oxygen, it may be assumed that the molecule of acid united to the latter oxygen persists in the double salts, which may be represented by the formula II (compare Favorski, A., 1913, i, 1146). T. H. P.

Dimethylpyrone. II. Adolf Baeyer and Jean Piccard (*Annalen*, 1915, **407**, 332—369. Compare A., 1911, i, 901).—[With Wolfgang Gruber.] 4-Methoxy-2 : 6-dimethylpyroxonium perchlorate (Baeyer, A., 1910, *i*, 763) is more easily prepared by warming dimethylpyrone, methyl sulphate, and a small quantity of methyl alcohol at 50°, and treating the resulting yellow syrup at 0° with 20% perchloric acid. An aqueous solution of the perchlorate, unlike those of 2 : 4 : 6-trimethyl- and 4-phenyl-2 : 6-dimethyl-pyroxonium perchlorates (Baeyer and Piccard, *loc. cit.*), is neutral to litmus, and therefore is not hydrolytically dissociated. Nevertheless, its electrical conductivity is as great as that of an equivalent solution of the 4-methoxylutidine perchlorate. This furnishes a proof of the quadrivalent character of the pyroxonium oxygen atom.

The methyl ether of the enolic form of diacetylacetone (Baeyer, *loc. cit.*) yields a yellow *sodium* derivative, and, contrary to the earlier statement, develops a brownish-red coloration with ferric chloride; it therefore slowly enolises.

The *sodium* derivative, yellow needles, of δ-methyl-Δγ-heptene-βζ-dione (Baeyer and Piccard, *loc. cit.*), obtained from the diketone and aqueous sodium hydroxide in the cold, is instantly decolorised by dilute perchloric acid. The resulting dienol partly changes to the ketonic form and is partly converted into 2 : 4 : 6-trimethylpyroxonium perchlorate. When the preceding sodium derivative is heated with aqueous sodium hydroxide on the water-bath for a few seconds and is then acidified with dilute perchloric acid, the trimethylpyroxonium

perchlorate is not obtained, but *m*-5-xylenol (identified as the tribromo-derivative, m. p. 164—167°).

δ-Methylheptane-$\beta\zeta$-dione (Baeyer and Piccard, *loc. cit.*), D_4^{23} 0·940, is converted by ethereal hydrogen chloride or by sodium ethoxide into Knœvenagel's 1 : 5-dimethyl*cyclo*hexen-3-one, the semicarbazone of which is also obtained by boiling the disemicarbazone of the saturated diketone with hydrochloric acid. When heated with a concentrated alcoholic solution of ammonia or of methylamine, the diketone and also the *cyclo*hexenone yield 3-*imino*- and 3-*methyl-imino*-1 : 5-*dimethyl*cyclo*hexene* respectively, of which the latter forms a *picrate*, prisms, m. p. 150—152°, and a crystalline *platinichloride*, $C_{18}H_{32}N_2PtCl_6$. The diketone, but not the *cyclo*hexenone, also reacts with hydrazine hydrate to form a substance which appears to be 1-aminodihydrocollidine; the *picrate* has m. p. 101·5—102°.

As stated by Feist and by Collie, dimethylpyrone is not reduced by zinc dust and glacial acetic acid. However, reduction ensues and a bluish-violet coloration is produced by the addition of concentrated hydrochloric acid. With zinc dust the colour is developed only at quite definite concentrations of the reagents, but magnesium powder produces it under all conditions, best in a dilute solution of dimethylpyrone in glacial acetic acid containing a trace of water, at the ordinary temperature. The reaction is extremely sensitive. The coloured substance has not been isolated, but some of its salts have been prepared; *perchlorate*, $C_{14}H_{16}O_2,HClO_4$, black or blackish-violet needles with a green, metallic reflex; *sulphate*, $C_{14}H_{16}O_2,H_2SO_4$, blue needles, prepared by oxidising the following leuco-compound with hydrogen peroxide and 20% sulphuric acid.

When dimethylpyrone is reduced by magnesium powder, glacial acetic acid, and methyl alcohol in the absence of air, a by-product of high molecular weight is obtained, together with the *leuco* compound of the preceding coloured base. The *leuco*-compound, $C_{14}H_{18}O_2$, yellow leaflets, m. p. 180—185°, can be sublimed, does not react with alkalis, ammonia, potassium, cold benzoyl chloride, or phenylhydrazine, but is rapidly oxidised in acetone solution by air in the presence of an aqueous mineral acid. In glacial acetic acid solution in an atmosphere of carbon dioxide, the leuco-compound is converted by two atomic proportions of bromine into the colour-base, and by four into a *dehydro*-derivative, which is colourless and unstable, but appears to have the composition $C_{14}H_{14}O_2 \pm xH_2O$.

By shaking the blue sulphate with 30% hydrogen peroxide at −15° and subsequently allowing the temperature to rise to 25°, two *ketones* are obtained. The main product is a *ketone*, $C_{14}H_{14}O_4$, colourless needles, m. p. 141—142°, which forms a *disemicarbazone*, $C_{16}H_{20}O_4N_6$, m. p. 261°, and *dioxime*, m. p. 245—246° (decomp.), and reacts with magnesium phenyl bromide to form ultimately a *substance*, $C_{20}H_{20}O_4$, leaflets, m. p. 130—131°. The by-product is a *ketone*, $C_{14}H_{14}O_4$, m. p. 92—94°, which forms a disemicarbazone identical with the preceding, and from which the ketone, m. p. 141—142°, is obtained by hydrolysis.

The ketone, m. p. 141—142°, is converted by methyl-alcoholic

potassium hydroxide into a *ketone*, $C_{13}H_{12}O_3$, m. p. 214°, which forms a *disemicarbazone*, and an oxonium *perchlorate*,

$$C_{13}H_{12}O_3,HClO_4,H_2O,$$

m. p. 230°. The ketone, m. p. 141—142°, is oxidised by chromic and acetic acids below 25° to an *acid*, $C_8H_8O_4$, m. p. 111°, which forms an *ethyl* ester, colourless prisms, m. p. 128°, and a *phenylhydrazone*, m. p. 222°; in alcoholic solution the acid is reduced by hydrogen and palladium black to an *acid*, $C_8H_{12}O_3$, colourless needles, m. p. 187°, an intermediate *compound*, $C_8H_{10}O_4$, m. p. 110—112° and 175° after resolidifying, also being isolated. C. S.

Organic Oxonium Compounds. I. Dimethylpyrone Hydrochloride. H. N. K. Rördam (*J. Amer. Chem. Soc.*, 1915, **37**, 557—567).—Although considerable evidence has accumulated indicating that the additive compounds of dimethylpyrone with acids are oxonium salts, stringent proof has not hitherto been obtained. It occurred to the author that the question could be decided by measuring the concentrations of hydrogen and chlorine ions in an aqueous solution of dimethylpyrone hydrochloride. If the compound merely dissociates, $C_7H_8O_2,HCl \rightleftarrows C_7H_8O_2 + HCl$, the concentrations of the hydrogen and chlorine ions would be equal, whereas if the product is a true salt the chlorine ion concentration would be greater than that of the hydrogen ions since, in addition to the chlorine ions from the free acid, there would also be chlorine ions derived from the salt: $C_7H_8O_2,HCl \rightleftarrows C_7H_8O_2{\cdot}H^{\cdot} + Cl'$.

Determinations have therefore been made of the chlorine ion concentration and conductivity of solutions of dimethylpyrone hydrochloride and of hydrochloric acid. The results show that in solutions which have the same chlorine ion concentration the molar conductivity of the dimethylpyrone hydrochloride solution is smaller than that of the hydrochloric acid, thus demonstrating that in the former solution the rapidly migrating hydrogen ions have been partly replaced by the much more slowly migrating dimethylpyrone ions. It is therefore evident that, in aqueous solutions of dimethylpyrone hydrochloride, electrolytic dissociation of the non-hydrolysed portion of the compound takes place, proving that the hydrochloride is a true salt.

The dissociation constant of dimethylpyrone as a base has been calculated and found to be $1{\cdot}9 \times 10^{-14}$, which agrees fairly well with the value, $2{\cdot}4 \times 10^{-14}$, obtained by Walden (A., 1902, i, 170) from conductivity measurements of the picrate.

Dimethylpyrone hydrochloride is therefore correctly represented by the oxonium formula. E. G.

Formation of Coumarin Derivatives, and the Preparation of Stable Coumarinic Acids. L. A. Jordan and J. F. Thorpe (T., 1915, **107**, 387—406).—The neutral substance obtained as a by-product by the action of alcoholic sodium ethoxide on ethyl *iso*dehydracetate (T., 1912, **101**, 1565) is now shown to be *ethyl 3-acetyl-4 : 5 : 7-trimethylcoumarin-6 : 8-dicarboxylate*, as on complete hydrolysis it is converted into *4 : 5 : 7-trimethylcoumarin*, the synthesis of which from *m*-5-xylenol and ethyl acetoacetate was accomplished by Clayton

(T., 1908, **93**, 2020). Ethyl acetyltrimethylcoumarindicarboxylate crystallises in needles, m. p. 135°, b. p. 253°/18 mm.; it gave no coloration with ferric chloride, but by treatment with aqueous alkali hydroxide it was converted into a salt of the corresponding *α-acetyl*-3 : 5-*dicarbethoxy*-*β*-4 : 6-*trimethylcoumarinic acid*, m. p. 146°, which gave a purple colour with ferric chloride. This and the other substituted coumarinic acids described below are characterised by remarkable stability, and a comparison shows that this stability decreases with a decrease in the number of substituents in the benzene nucleus, and is greatest when position 8 is occupied by the carboxyl group, and, moreover, it appears to be the acidity rather than the weight of the group which is the determining factor. From the above acetylcoumarin the acetyl group was eliminated by means of alcohol and sulphuric acid, and *ethyl* 4 : 5 : 7-*trimethylcoumarin*-6 : 8-*dicarboxylate* was produced. It crystallises in concentric needles, m. p. 131°, and when warmed with dilute aqueous potassium hydroxide, it was converted after acidification into its corresponding 3 : 5-*dicarbethoxy*-*β* : 4 : 6-*trimethylcoumarinic acid*, crystallising in plates, m. p. 122°. Heated above its melting point the acid passed into the coumarin. Towards fused caustic alkali the original acetylcoumarin, m. p. 135°, is exceptionally stable, the only result of this treatment being the hydrolysis of one carbethoxy-group with the production of *α-acetyl*-3-*carboxy*-5-*carbethoxy*-*β*-4 : 6-*trimethylcoumarinic acid*, m. p. 176°, from which on heating above its melting point the coumarin, 6-*ethyl* 8-*hydrogen* 3-*acetyl*-4 : 5 : 7-*trimethylcoumarin*-6 : 8-*dicarboxylate*, m. p. 235°, was obtained. These two compounds were de-acetylated by treatment with alcohol and sulphuric acid, and 3-*carboxy*-5-*carbethoxy*-*β*-4 : 6-*trimethylcoumarinic acid*, forming white needles, m. p. 129°, was formed in each case. It is so stable that it cannot be converted into the corresponding coumarin. On heating with water at 180° for five hours, carbon dioxide was eliminated, and 6-*carbethoxy*-4 : 5 : 6-*trimethylcoumarin* resulted. This substance forms small needles and melts at 124°. It dissolves in alkali hydroxides, but is reprecipitated on the addition of acids, and the effect of the absence of the carboxyl group in position 8 on the stability of the corresponding coumarinic acid is thus obvious. The partial hydrolysis of the original, fully substituted coumarin, m. p. 135°, with 50% sulphuric acid gave a mixture of 4 : 5 : 7-trimethylcoumarin and 3-*carboxy*-*β*-4 : 6-*trimethylcoumarinic acid*, which were separated by treatment with sodium carbonate solution. The acid forms slender needles, m. p. 300°. When heated above this temperature it does not lose water to form the corresponding coumarin, but carbon dioxide is evolved and it passes into 4 : 5 : 7-trimethylcoumarin. The exceptional stability of this acid is due to the free 8-carboxyl group, for when the *diammonium* salt was boiled it lost ammonia and the solution then contained the neutral salt of the coumarin, and silver nitrate precipitated the *silver* salt of the coumarin. When, however, the free carboxyl group was regenerated from either of these salts, it was the coumarinic acid, m. p. 300°, which was obtained and not the coumarin. The above silver salt was transformed into the *ethyl* ester, m. p. 133°, which, also, with warm sodium hydroxide gave the original coumarinic acid. 4 : 5 : 7-*Trimethylcoumarin*, the final product of hydrolysis, forms

laminæ, m. p. 178°. It dissolves in warm sodium hydroxide, and when the solution is acidified at 0°, the *β*-4 : 6-*trimethylcoumarinic acid* is precipitated. It forms needles, m. p. 128°, and is so unstable that on boiling with water or on keeping at ordinary temperatures it is completely converted into the coumarin.

The action of phosphorus pentachloride on a solution of the original fully substituted coumarin in phosphoryl chloride was to produce first a purple solution from which ether precipitated a blue phosphorus-containing solid which was very unstable in moist air and probably had a composition similar to that of the crystalline precipitate obtained with coumarin itself, viz., an additive compound of phosphorus trichloride and the chloro-acid chloride of the coumarinic acid. On treatment with alcohol, *ethyl* 2-*chloro*-*α*-*acetyl*-3 : 5-*dicarbethoxy*-*β*-4 : 6-*trimethylcinnamate* was obtained. The action of bromine on the original coumarin produced *ethyl* 3-*bromo*-4 : 5 : 7-*trimethylcoumarin*-6 : 8-*dicarboxylate*, the acetyl group being eliminated. This forms small needles, m. p. 114°, which on treatment with boiling alcoholic potassium hydroxide were converted into 4-*carbethoxy*-6-*carboxy*-2 : 3 : 5-*trimethylcoumarilic acid*, colourless flakes, m. p. 197°. Similarly, 4 : 5 : 7-trimethylcoumarin absorbed bromine in chloroform solution, giving 3-*bromo*-4 : 5 : 7-*trimethylcoumarin*, m. p. 163°, which was likewise converted by alkali into 2 : 3 : 5-*trimethylcoumarilic acid*, m. p. 149°.

The nitration of 4 : 5 : 7-trimethylcoumarin leads to the formation of 6-*nitro*-4 : 5 : 7-*trimethylcoumarin*, colourless needles, m. p. 208°. The corresponding coumarinic acid could not be isolated. Further nitration gave 3 : 6 : 8-*trinitro*-4 : 5 : 7-*trimethylcoumarin*, cream-coloured needles, m. p. 225°, which by the action of alkali was converted into *ω*-3 : 5-*trinitro*-2-*hydroxy*-*α*-4 : 6-*trimethylstyrene*, crystallising from benzene in nodules, m. p. 103°. Nitration of the fully-substituted coumarin resulted in the formation of *ethyl* 6-*nitro*-4 : 5 : 7-*trimethylcoumarin*-8-*carboxylate*, colourless needles, m. p. 170°. The acetyl group was thus displaced, but its position was not substituted, the nitro-group replacing a carbethoxy-group instead. The coumarinic acid was unstable, and could not be isolated.

All the above-described coumarins dissolve in alkali to form colourless solutions of the salt of coumarinic acid; this appears characteristic of 4-substituted coumarins, in contradistinction to unsubstituted coumarinic acid, which gives yellow alkali salts. A fundamental structural difference is consequently inferred, and the constitution of the coumarinic acids from this standpoint is discussed. The mobility of the hydrogen atom in the system C:C·CH depends on the presence or absence of a group on the central carbon atom, as evidenced by the glutaconic acids for example, and hence for the salts of the unsubstituted coumarinic acids an ortho-quinonoid structure,

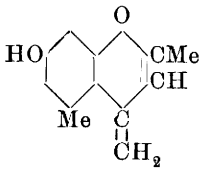
$$O:C_6H_4:CH\cdot CH_2\cdot CO_2Na,$$

is suggested, whilst the colourless 4-substituted coumarinates would have the normal *cis*-formula $OH\cdot C_6H_4\cdot CMe:CH\cdot CO_2Na$. G. F. M.

Some Benzopyranol Derivatives. J. N. Collie and G. N. White (T., 1915, **107**, 369—376).—Under the influence of con-

centrated mineral acids, orcinol condenses with acetylacetone to give a mixture of the salts of two benzopyranols, which can be separated by fractional crystallisation from aqueous hydrochloric or hydrobromic acids.

7-*Hydroxy*-2 : 5-*dimethyl*-4-*methylene*-γ-*benzopyranol* is an orange substance; it gives a lemon-yellow *hydrochloride*, a greenish-yellow *hydrobromide*, and *platini-* and *platino-chlorides*. The base dissolves in sodium hydroxide, giving a pale yellow solution, and gives a colourless *acetyl* derivative.



5-*Hydroxy*-2 : 7-*dimethyl*-4-*methylene*-γ-*benzopyranol* is a violet substance, giving an orange *hydrochloride* and *hydrobromide*, and *platini-* and *platino-chlorides*. It also gives a colourless *acetyl* derivative, and dissolves in sodium hydroxide to an almost colourless solution.

Although *dihydro-* and *tetrahydro*-derivatives were obtained, yet neither of the bases is readily reduced, a fact which speaks against the possible alternative quinonoid constitution, as does also the non-formation of oximes, phenylhydrazones, and semicarbazones. On the other hand, the displacement of the hydroxyl group in the benzene nucleus by the acetoxyl group entirely destroys the basic character of the pyranol nucleus, and the two bases having the same chromophoric system should be similarly coloured. It is suggested as the best explanation, that the bases and their salts are quinonoid, but that the colourless acetates are benzenoid. If acids then favour the quinonoid form, bases should promote the formation of the hydroxyl form, hence the almost colourless solutions in sodium hydroxide and the absence of oxime formation, etc., with hydroxylamine. G. F. M.

Double Halogen Salts of Quinine and Carbamide. II. P. G. Golubev (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 14—17. Compare A., 1914, i, 719).—The *double hydriodide* of quinine and carbamide, $C_{20}H_{24}O_2N_2,CH_4ON_2,2HI,5H_2O$, forms long, thin, bright yellow, prismatic crystals, m. p. 62—64°, which rapidly effloresce in the air. When heated at 100°, it decomposes according to the equation:

$$C_{22}H_{24}O_2N_2,CH_4ON_2,2HI + H_2O = C_{20}H_{24}O_2N_2,2HI + CO_2 + NH_3,$$

but excess of cold water removes the carbamide and part of the hydriodic acid, *quinine sesquihydriodide*, $C_{20}H_{24}O_2N_2,1\frac{1}{2}HI$, being deposited in white, silky, thread-like crystals, m. p. 42—45°.

T. H. P.

Histidine. A. Kossel and S. Edlbacher (*Zeitsch. physiol. Chem.*, 1915, **93**, 396—400).—Benzoylation of histidine methyl ester yields the tribenzoyl product,

$$CH(NHBz):C(NHBz)\cdot CH_2\cdot CH(NHBz)\cdot CO_2Me,$$

which forms long needles, m. p. 219° (not sharp). It does not give a coloration with diazobenzenesulphonic acid (compare Windaus, A., 1910, i, 283), but on heating the glyoxaline ring closes again and the product gives a red coloration with diazobenzenesulphonic acid and alkali. This explains the observations of Inouye (A., 1913, ii, 164).

Carnosine, which is a compound of histidine and β-alanine, behaves like histidine.

Glyoxaline reacts with formaldehyde, one nitrogen atom being almost completely (84—85%) involved. Alanine also has a nitrogen atom which reacts with formaldehyde (Sörensen). Regarding histidine, which is a glyoxalylalanine, discordant statements have been made. The authors find that 116—133% of the calculated amount of formaldehyde for one nitrogen atom is used. If histidine methyl ester is used, 174—200% is obtained, showing that the presence of a free carboxyl group reduces the reactivity towards formaldehyde.

R. V. S.

Crystalline Calcium Theobrominate. Louis Rousseau (*Compt. rend.*, 1915, **160**, 363—365).—The author has prepared a crystalline calcium theobrominate, $(C_7H_7O_2N_4)_2Ca,9H_2O$, by boiling calcium hydroxide (1 mol.) with theobromine (2 mols.) in water, free from carbon dioxide. On cooling the solution the theobrominate crystallised in long, slender needles. This substance loses its water of crystallisation with difficulty at 120°. It is far more soluble in water and alcohol than theobromine. It is decomposed by carbon dioxide, regenerating theobromine, and on decomposition by dilute acids yields theobromine in the colloidal state. W. G.

Phosphoric Acid Esters of Methylglucoside and Theophyllineglucoside. Emil Fischer (*Ber.*, 1914, **47**, 3193—3205).—The preparation of purine glucosides (A., 1914, *i*, 333) foreshadowed the synthesis of nucleic acids (nucleotides) which has now been successfully accomplished in the case of theophyllineglucoside-phosphoric acid. The difficulty to be overcome was the combination of phosphoric acid with the glucose residue. The only available methods of any promise were the application of phosphoryl chloride in the presence of aqueous suspensions of alkaline earths or their carbonates (Neuberg and Pollak, A., 1910, i, 157, 610) and the use of metaphosphoric esters in chloroform or without a solvent (Langheld, A., 1910, i, 536; 1912, i, 415). Both methods were tried in the case of α-methylglucoside and theophyllineglucoside. The former method gave poor yields owing to the decomposition of the oxychloride by the water, whilst the latter method cannot be applied to solid glucosides since they are usually insoluble in chloroform. A valuable process was finally discovered in the use of phosphoryl chloride and pyridine which is a good solvent for sugars and glucosides. In this way, a crystalline phosphoric acid derivative of the theophyllineglucoside has been obtained in excellent yield. It is not identical with the acid obtained by the action of the oxychloride in the presence of baryta.

The combination phosphoryl chloride and pyridine is also worthy of adoption in the case of the simple sugars and even sucrose (future communication), but it is not applicable to the amino-acids or inositol, since these do not dissolve readily enough in the base. The method will be extended to the other purine glucosides and naturally occurring nucleosides and then the interesting problem of the fate of these synthetic nucleotides in the organism will be attacked.

The crystalline theophyllineglucosidephosphoric acid titrates as a monobasic acid, but changes under the influence of bases into an amorphous dibasic acid. The crystalline substance is therefore a secondary ester, and its transformation into a primary ester is not remarkable in view of the experience of Grün and Kade with the stearin phosphates (A., 1912, i, 158).

Perfectly dry theophyllineglucoside was dissolved in dry pyridine, cooled to $-20°$ and treated with a cold mixture of phosphoryl chloride (1 mol.) and pyridine. After an hour, the mixture was cautiously treated with cold water, shaken with silver sulphate, and after removing the excess of silver, the filtrate was evaporated under reduced pressure at 40° with barium hydroxide until free from pyridine. The excess of baryta was removed by carbon dioxide and the mixture was then evaporated again to a small bulk and filtered into absolute alcohol. The precipitated barium salt was finally decomposed exactly by sulphuric acid. The yield of the acid was about 45%, calculated on the original glucoside. *Theophyllineglucosidephosphoric acid*,

$$C_{13}H_{16}O_7N_4\cdot PO_2H,2H_2O,$$

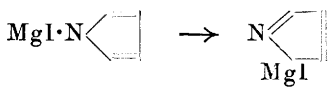
crystallises from water in slender needles or long leaflets, $[\alpha]_D^{26} - 29{\cdot}76°$. It is bitter, gives the murexide test with chlorine water, reduces Fehling's solution feebly and gives no precipitates with tannin or egg albumin. With aqueous phosphotungstic acid it gives a yellow coloration, but with a solution of phosphotungstic acid in 10—20% sulphuric acid, it gives a deep yellow precipitate. The *mono-barium* salt is amorphous. The hydrolysis of the acid by more than 7% hydrochloric acid was very complicated, but phenylglucosazone and pure theophylline were isolated when a 1% acid was employed, although many unknown by-products were obtained even in this case.

An amorphous *di-barium* salt was obtained by treating the glucoside with phosphoryl chloride, baryta and water at 0°, and, after removing the chlorine as before, heating the filtrate with baryta, removing the excess by carbon dioxide, evaporating the filtrate, and precipitating the residue by alcohol.

Less satisfactory results were obtained in the case of α-methylglucoside. Using ethyl metaphosphate (Langheld), a *barium* salt of a tetrabasic methylglucosidediphosphoric acid, $C_7H_{12}O_6(PO_3Ba)_2$, was isolated, whilst the pyridine method gave an impure *di-barium* salt of a monophosphoric acid, $C_7H_{13}O_9PBa$, insoluble in alcohol, and the baryta method a barium salt which was somewhat soluble in alcohol. J. C. W.

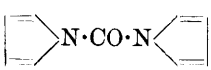
Isomerism of the Organo-metallic Compounds of Pyrrole under the Action of Ethyl Chlorocarbonate and Ethyl Carbonate. V. V. Tschelincev and S. G. Karmanov (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 161—169).—When potassiopyrrole is treated with alkyl haloids, it yields principally 1-pyrrole derivatives, whilst with chloroanhydrides of acids, roughly equal proportions of 1- and 2-substituted pyrroles are obtained, and, with anhydrides, mainly the 2-derivatives. Since Ciamician and Magnaghi (A., 1885, 1143) showed that 1-derivatives of pyrrole may be converted into the corresponding 2-derivatives (compare Pictet, A., 1904, i, 771), it has

been supposed that those reactions in which the latter are formed yield first the 1-compounds, these then undergoing isomerisation. Owing to the fact that this change is not quantitative, it became necessary to assume that the isomerisation takes place with the organometallic compound before removal of the metal. Terentev (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1399) considers the conversion to be accompanied by isomerisation of the annexed pyrrole ring itself.



In the case of the Grignard reagent, Hess and Wissing (A., 1914, i, 725) find the action to be the same with 1-methylpyrrole as with pyrrole, and these authors draw the conclusion that the bromomagnesium group enters, in both cases, the 2-position, and thus gives rise to compounds essentially different from potassiopyrrole, in which the metal occupies the 1-position.

This conclusion may be true in so far as the bromo-magnesium derivatives of 1-substituted pyrroles are concerned, but the authors' experiments show that the interaction of magnesium pyrryl bromide and ethyl chlorocarbonate and decomposition of the resultant product by means of water yield almost exclusively ethyl pyrrole-2-carboxylate, whilst with ethyl carbonate under similar conditions the products obtained are: (1) principally ethyl pyrrole-1-carboxylate; (2) a very small proportion of a crystalline compound, m. p. 56°, which is possibly impure carbopyrride (annexed formula), formed by the action of magnesium 1-pyrryl bromide on (1); (3) a small proportion of a liquid, possibly the pyrrole-2-carboxylic ester.



It may be concluded, therefore, that no fundamental difference exists between the potassium and magnesium derivatives of pyrrole, and it seems probable that each consists of a mixture of 1- and 2-substituted molecules. Whether this mixture yields derivatives with the substituent in the 1- or in the 2-position depends on the relation between the initial compounds and the nature of the reagent, and, possibly, on differences in the velocities of reaction with the two isomeric molecules; it is evident, however, that the magnesium derivative tends to form 2-compounds, and the potassium derivative, 1-compounds the more readily. T. H. P.

Cyclic Hydroxylamine Derivatives. P. Friedländer (*Ber.*, 1914, **47**, 3369—3370).—The assertions of Heller and Wunderlich (*Ber.*, 1914, **47**, 2889) that *N*-hydroxy-compounds have not been previously obtained in the quinoline series and of Reissert (A., 1896, i, 389) that 1-hydroxyindole-2-carboxylic acid is the first representative of substances containing the :N·OH group as a member of a ring are not accurate. In conjunction with Ostermaier (A., 1882, 201) the author has previously described a compound, obtained by the reduction of *o*-nitrocinnamic ester with alcoholic ammonium sulphide, which must contain the group –NO:C·OH– or –N(OH)·CO–, and for which the latter formulation is preferred on account of the relatively difficult hydrolysis of the corresponding ethyl ether. H. W.

The Preparation of Potassium Indoxyl Sulphate. AD. JOLLES and ERW. SCHWENK (*Biochem. Zeitsch.*, 1915, **68**, 347—349).—A preliminary account of a method for preparing this substance is given, the essential of which is the treatment of *N*-acetylindoxyl with chlorosulphonic acid in pyridine solution. S. B. S.

Isatin and its Derivatives. II. Isatoxime → *o*-Cyanophenylcarbimide and Related Reactions. W. BORSCHE and W. SANDER (*Ber.*, 1914, **47**, 2815—2826. Compare Borsche and Jacobs, A., 1914, i, 322).—In an endeavour to produce with isatoxime a change analogous to that observed in the formation of α-hydroxycinchoninic acid from isatin, malonic acid and acetic acids (*loc. cit.*), the authors have attempted to produce a quinoxaline or quinazoline ring by submitting isatoxime to the Beckmann rearrangement, but the product of the action of phosphorus pentachloride was *s*-di-*o*-cyanophenylcarbamide resulting from *o*-cyanophenylcarbimide; the latter owes its formation to the successive changes

$$C_6H_4\langle\begin{matrix}C(:NOH)\\NH\end{matrix}\rangle CO \longrightarrow C_6H_4\langle\begin{matrix}C(:NCl)\\NH\end{matrix}\rangle CO \longrightarrow$$

$$C_6H_4\langle\begin{matrix}C:N\\NH\cdot COCl\end{matrix} \longrightarrow CN\cdot C_6H_4\cdot NCO.$$

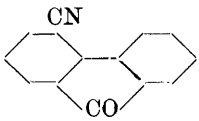
The accuracy of this view is indicated by the isolation of *o*-cyanophenylcarbimide when isatoxime is distilled with phosphorus pentachloride under reduced pressure, and the interaction of 1-methylisatoxime with phosphorus pentachloride in an analogous manner yields *o*-cyanophenylmethylcarbamyl chloride, $CN\cdot C_6H_4\cdot NMe\cdot COCl$; several other compounds of a similar type have also been submitted to distillation with phosphorus pentachloride.

Isatoxime, for which the m. p. was found to be 216—217° (decomp.), was converted by treatment with methyl sulphate and sodium hydroxide into 1-*methylisatoxime methyl ether*, $C_6H_4\langle\begin{matrix}C(:NOMe)\\NMe\end{matrix}\rangle CO$, deep yellow needles, m. p. 147—148°, whilst the action of ethyl sulphate gave only the mono-ethyl derivative, isatoxime ethyl ether, $C_6H_4\langle\begin{matrix}C(:NOEt)\\NH\end{matrix}\rangle CO$. When treated with phosphorus pentachloride, isatoxime gave a product which reacted with water, yielding *s-di-o-cyanophenylcarbamide*, $CO(NH\cdot C_6H_4\cdot CN)_2$, needles which decompose near 250°. When the reaction product from a suspension of isatoxime and phosphorus pentachloride was submitted to distillation under reduced pressure, *o-cyanophenylcarbimide* was obtained as a liquid, b. p. 124°/13 mm., which solidified to a crystalline mass, m. p. 61°. This substance resembles phenylcarbimide in its effect on the mucous membrane and also shows similar chemical behaviour, giving *ethyl o-cyanophenylcarbamate*, $CN\cdot C_6H_4\cdot NH\cdot CO_2Et$, prisms or needles, m. p. 107°, and *o-cyanocarbanilide*, $CN\cdot C_6H_4\cdot NH\cdot CO\cdot NHPh$, needles, m. p. 163°, with alcohol and aniline respectively in benzene solution.

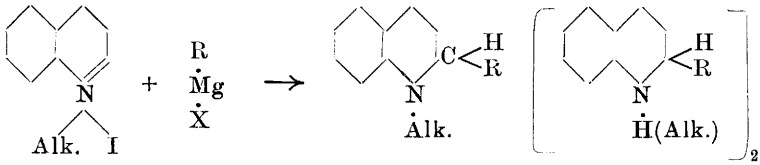
1-Methylisatoxime, yellow needles, m. p. 196—198°, on methylation by methyl iodide and sodium methoxide in methyl-alcoholic solution, yielded the 1-methylisatoxime methyl ether already described. The reaction product from an ethereal suspension of 1-methylisatoxime and

phosphorus pentachloride on distillation gave *o-cyanophenylmethylcarbamyl chloride*, $CN\cdot C_6H_4\cdot NMe\cdot COCl$, b. p. 180°/15 mm., m. p. 60°, which reacted with a benzene solution of aniline, producing *o-cyanomethylcarbanilide*, $CN\cdot C_6H_4\cdot NMe\cdot CO\cdot NHPh$, needles, m. p. 186°.

Thionaphthenquinone-β-oxime, when treated with phosphorus pentachloride in the usual manner, gave *o-cyanophenyl sulphur chloride* [*o-chlorothiolbenzonitrile*], $CN\cdot C_6H_4\cdot SCl$, a deep yellow, viscous liquid, b. p. 145—150°/16 mm. Under similar treatment, α-nitroso-β-naphthol gave a distillate of *o-cyanocinnamoyl chloride*, $CN\cdot C_6H_4\cdot CH{:}CH\cdot COCl$, yellow needles, m. p. 91°; 3-nitroso-β-naphthol produced *ω-cyanostyrene-o-carboxylic acid chloride*, $CN\cdot CH{:}CH\cdot C_6H_4\cdot COCl$, colourless needles, m. p. 83°. Phenanthraquinone monoxime yielded 4-cyanofluorenone (annexed formula), yellow needles, m. p. 240°, resulting from elimination of hydrogen chloride from the primarily formed *o*-cyanodiphenyl-*o'*-carboxylic acid chloride, $CN\cdot C_6H_4\cdot C_6H_4\cdot COCl$. D. F. T.



Dihydroquinaldine Bases. Gustav Heller (*Ber.*, 1914, **47**, 2893—2902).—2-Methyldihydroquinoline bases are produced in accordance with scheme (I).



(I.) (II.)

In presence of nascent hydrogen the initially formed unimolecular dihydro-bases are catalysed to bimolecular compounds (II), a new type of reaction, and one not effected by molecular or ionic hydrogen.

[With L. Bub and Max Kopetzky.]—Bimolecular 1 : 2-*dimethyldihydroquinoline* is formed from the *pseudo*-base precipitated by sodium hydroxide from 2-methylquinoline methiodide by reduction with zinc and hydrochloric acid. It is a weak base, but stronger than 2-methyldihydroquinoline, and melts at 179—180°. It is also produced by reduction of the iodide derivative directly in solution in hydrochloric acid, in presence of sodium chloride, but the product is not so readily purified or freed from halogen. It is not reduced by sodium and alcohol, or tin and hydrochloric acid. A solution in glacial acetic acid is oxidised by chromic acid, but no definite product has been isolated.

Bimolecular 2-*methyl*-1-*ethyldihydroquinoline* is prepared similarly from 2-methylquinoline ethiodide as an amorphous precipitate. A small amount of a by-product can be extracted from the zinc residue by absolute alcohol, and forms needles, m. p. 186—187°. Bimolecular 2-*methyl*-1-*propyldihydroquinoline* is formed from the corresponding propyl derivative, and has m. p. 166—167°. A trace of by-product can be isolated in four-sided prisms, m. p. 187°. Reduction of **2** : 4-

dimethylquinoline methiodide, m. p. 226°, and extraction of the zinc residue yields 1 : 2 : 4-*trimethyldihydroquinoline*, colourless needles, m. p. 252°. Amorphous products are formed by reduction of the methyl and ethyl chloride derivatives of quinoline.

Quinoline bases with acidic groups are not reduced under the conditions described, examples being carbostyril, α-hydroxylepidine, α-methylcinchonic acid, and quinoline-2-carboxylic acid.

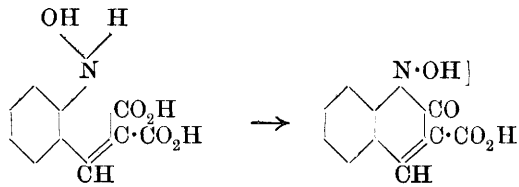
Reduction of 2 : 4-dimethylquinoline produces a small proportion of an amorphous product. From the zinc residue, alcohol extracts bimolecular 2 : 4-*dimethyldihydroquinoline*, m. p. 176°, a substance of weak basic properties. Chromic acid converts it into 2 : 4-dimethylquinoline chromate, m. p. 172°.

4-Chloro-2-methylquinoline is reduced to an unidentified *base*, free from chlorine, and sodium acetate precipitates another *base* of unknown constitution, which forms a picrate. The zinc residue from the reduction of 2-phenylquinoline yields a colourless, crystalline *substance*, m. p. 170°. *iso*Quinoline is not reduced by zinc and hydrochloric acid.

Reduction of 2-phenylquinoline methiodide by hydrochloric acid and zinc in presence of sodium chloride precipitates a colourless, amorphous, weakly basic *substance*. From the acid filtrate, sodium acetate precipitates a small amount of 2-phenyl-1-methyltetrahydroquinoline, identical with that prepared by Freund's method (A., 1905, i, 151; 1909, i, 417). It forms anthracene-like, pale blue, fluorescent leaflets, m. p. 102—103° (Freund, 106—107°). It is a weak base, but stronger than 2-phenyl-1-methyldihydroquinoline. Its solution in hydrochloric acid gives a blood-red coloration with sodium nitrite, addition of sodium acetate to the diluted solution precipitating a red, flocculent substance.

1 : 2-Dimethyldihydroquinoline, prepared by Freund's method (*loc. cit.*), and the corresponding ethyl derivative are converted by zinc dust and hydrochloric acid into bimolecular compounds identical with those previously described, the nascent hydrogen functioning as polymerising agent. A. J. W.

1-Hydroxycarbostyril-3-carboxylic Acid. Gustav Heller and Paul Wunderlich (*Ber.*, 1914, **47**, 2889—2893).—A description of 1-hydroxycarbostyril-3-carboxylic acid and its derivatives. On reduction with zinc dust and acetic acid, *o*-nitrobenzylidenemalonic acid (prepared by a slight modification of Stuart's method, T., 1885, **47**, 155) yields 1-hydroxycarbostyril-3-carboxylic acid (II.), with intermediate formation of *hydroxylaminobenzylidenemalonic acid* (I.):



(I.) (II.)

1-*Hydroxycarbostyril*-3-*carboxylic acid* forms colourless needles, m. p. 259—260° (decomp.). In aqueous and alcoholic solution it gives a dark red coloration with ferric chloride. It does not reduce Fehling's solution. Cotton mordanted with iron or titanium salts is dyed reddish-brown. Alkaline permanganate converts it into a mixture of *o*-nitrobenzoic acid and *o*-azoxybenzoic acid. When heated at its melting point with water, it forms carbostyril. The *sodium* salt crystallises in pale yellow leaflets, and the *silver* salt is golden-yellow.

Reduction in ammoniacal solution with ferrous sulphate transforms the 1-hydroxy-acid into carbostyril-3-carboxylic acid. With thionyl chloride it yields a semi-crystalline *chloride*, converted by aniline into the corresponding *anilide*, m. p. 264—265°. In alcoholic solution this anilide gives a red coloration with ferric chloride. In alkaline solution neither it nor the corresponding acid is attacked by hydrogen peroxide or potassium ferricyanide.

Methyl sulphate converts 1-hydroxycarbostyril-3-carboxylic acid into 1-*methoxycarbostyril*-3-*carboxylic acid*, colourless needles, m. p. 202—203°, which gives no coloration with ferric chloride. Acetylation with acetic anhydride of the *N*-hydroxy-acid in acetic acid solution produces 1-*acetoxycarbostyril*-3-*carboxylic acid*, needles, m. p. 202°.

A. J. W.

*iso*Quinoline in Coal Tar. R. Weissgerber (*Ber.*, 1914, **47**, 3175—3181).—*iso*Quinoline occurs to the extent of less than 1% in the crude quinoline obtained from coal tar, and was isolated from this source by Hoogewerff and van Dorp by fractional crystallisation of the hydrogen sulphates (A., 1886, 78). A process has now been devised for the extraction of *iso*quinoline on the large scale.

As might be expected from the fact that the nitrogen atom is farther removed from the benzene nucleus, *iso*quinoline is more basic than quinoline. Consequently, by shaking a benzene solution of the crude oil with enough 20% sulphuric acid to combine with about one-sixth of the base, the extract is considerably enriched in *iso*quinoline. The enriched base, recovered from the acid solution, is now fractionated, when a higher fraction, b. p. up to 260°, is removed. This consists, probably, of methylated pyridines. The quinoline fraction is then best separated by the old method. Apparently, the two quinolines are the only tar bases the sulphates of which are precipitated in alcoholic solution, so that the original crude tar-oil bases may be treated in this way with advantage, without troubling to isolate the crude quinoline first.

A further consideration of the constitution of *iso*quinoline would lead to the expectation that this base is more easily sulphonated than quinoline. This is the case, and α-*iso*quinolinesulphonic acid is easily isolated by adding the crude sulphates (above) to cold sulphuric acid containing 50% of the anhydride. It seems impossible to convert this into *iso*quinoline, however. In order to test the purity of the acid, it was fused with potassium hydroxide, whereby it was found that α-hydroxy*iso*quinoline is produced at 200—250°, but that a *dihydroxy*-iso*quinoline* is formed if the fusion is carried out at 300°. This compound is no longer basic, but dissolves in sodium carbonate and

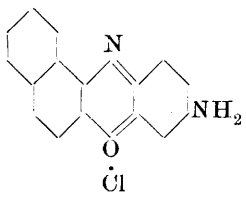
gives orange-red azo-dyes. It forms pale yellow needles from water, m. p. 273° (decomp.). J. C. W.

A Synthesis in the Group of the Oxazine Dyes. F. KEHRMANN and DORA KISSINE (*Ber.*, 1914, **47**, 3096—3100).—Since aminonaphtha-*o*-quinones condense with aminophenols to form derivatives of naphthaphenazoxonium, it was natural to expect that aminonaphthols would react to form dinaphthazoxonium compounds. 2 : 4-Diaminonaphthol oxidises too readily in the air, so 2-amino-4-acetylaminonaphthol was prepared and used to test this point.

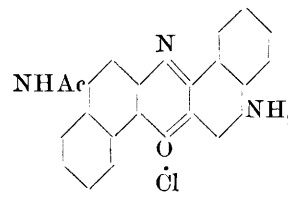
Diacetyl-1 : 4-aminonaphthol was partly hydrolysed by shaking with 10% sodium hydroxide, and the 4-acetylaminonaphthol,

$$OH\cdot C_{10}H_6\cdot NHAc,$$

colourless crystals, m. p. 178°, was converted into 2-*nitroso*-4-*acetylaminonaphthol*, $C_{12}H_{10}O_3N_2$, brownish-yellow crystals, decomp. 190°, and this was reduced by sodium sulphide. The *hydrochloride* of the 2-*amino*-4-*acetylaminonaphthol* formed long, pale grey needles, readily soluble in water but almost insoluble in dilute hydrochloric acid, and was immediately oxidised by ferric chloride to 4-acetylamino-1 : 2-naphthaquinone. The hydrochloride was boiled with 4-amino-1 : 2-naphthaquinone in methyl alcohol, when the *chloride* of the dinaphthazoxonium dye separated on cooling in bluish-violet needles. The chloride dissolves in water with Bordeaux-red colour, but undergoes partial hydrolysis to the free base, which is orange-yellow and insoluble. In its colour reactions, the dye resembles 3-aminonaphthaphenazoxonium chloride (I), and the new compound may therefore have the formula (II).



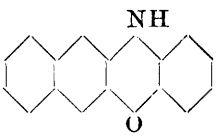
(I.)



II.)

J. C. W.

Synthesis in the Oxazine Group. F. KEHRMANN and ARCHIBALD A. NEIL (*Ber.*, 1914, **47**, 3102—3109).—I. *ββ-Naphthaphenoxazine.*—An intimate mixture of *o*-aminophenol and 2 : 3-dihydroxynaphthalene was gradually heated to 200° in a current of carbon dioxide, whereby steam was evolved at 140—150° and the mass solidified at 160—170°. The powdered product was boiled with small volumes of very dilute hydrochloric acid as long as the filtrate deposited crystals, when the dried residue was crystallised from a mixture of benzene and alcohol. This, the main product, namely, *benzo*-2 : 3-*phenazoxine* [*ββ-naphthaphenoxazine*] (annexed formula), formed colourless leaflets, m. p. 302°, which gave a magenta solution in concentrated sulphuric acid, whilst the above by-product,



namely, o-*hydroxyphenyl*-3-*hydroxy*-β-*naphthylamine*,

$$OH\cdot C_{10}H_6\cdot NH\cdot C_6H_4\cdot OH,$$

crystallised in colourless needles, m. p. 155—156°. The yield of the latter is greater if the temperature of the reaction is moderated. Naturally, the compound undergoes ring-condensation when heated above 200°. The naphthaphenoxazine is also formed if the hydrochloric acid solution is exposed to the air, which may be explained by the intervention of an *o*-quinonoid derivative and a phenazoxonium chloride, thus:

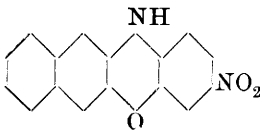
I. $OH\cdot C_{10}H_6\cdot NH\cdot C_6H_4\cdot OH + O \longrightarrow$

$$OH\cdot C_{10}H_6\cdot N{:}C_6H_4{:}O \xrightarrow{HCl} C_{10}H_6\langle{}^{N}_{O}\rangle C_6H_4.$$
$$\dot{C}l$$

II. $C_{10}H_6\langle{}^{N}_{O}\rangle C_6H_4 + OH\cdot C_{10}H_6\cdot NH\cdot C_6H_4\cdot OH =$
$$\dot{C}l$$

$$OH\cdot C_{10}H_6\cdot N{:}C_6H_4{:}O + C_{10}H_6\langle{}^{NH}_{O}\rangle C_6H_4.$$

The *acetyl* derivative of ββ-naphthaphenoxazine, m. p. 151°, was nitrated by fuming nitric acid in ice-cold glacial acetic acid, and gave a mixture of products. A dark red, explosive *tetranitro-ββ-naphthaphenoxazine* separated from the reaction mixture (solution in very dilute alkali hydroxide, violet; in concentrated sulphuric acid, blood-red), whilst the mother liquor deposited an orange-yellow substance on dilution. The latter was repeatedly warmed with very dilute alcoholic sodium hydroxide, which dissolved polynitro-compounds with a violet colour, and left a hydrolysed mononitro-derivative. The latter, probably 2-*nitro*-ββ-*naphthaphenoxazine* (annexed formula), formed very long, dark brownish-red, glistening needles, m. p. 222—223° (decomp.).



II. *Phenoxazine.* Catechol and *o*-aminophenol only condense to a slight extent when gently boiled together in an open vessel, but it is unnecessary to employ sealed tubes for the preparation of phenoxazine (Bernsthen, 1887), for good yields may be obtained by heating catechol and *o*-aminophenol with a little of the hydrochloride of the latter, or even by heating *o*-aminophenol with its own hydrochloride at 240°.

The colourless mother liquors of many phenoxazines as obtained by the old condensations regularly developed violet colours and then deposited much more of the phenoxazine than mere evaporation would warrant (see A., 1902, i, 566). This is now explained by the presence in the mother liquors of the intermediate products analogous to the above *o*-hydroxyphenyl-3-hydroxy-2-naphthylamine. J. C. W.

Phenazthionium Salts. F. Kehrmann and Louis Diserens (*Ber.*, 1915, **48**, 318—328).—Certain discrepancies between the older observations of the author (A., 1902, i, 186) and those of Pummerer and Gassner (A., 1913, i, 991; 1914, i, 735) have been examined.

Uniform products are not obtained by the action of bromine on thiodiphenylamine in alcoholic solution, and the use of this solvent has been described in error. In ethereal or glacial acetic acid solution, on the other hand, a dark green bromide is easily prepared, which was formerly regarded as the normal *holo*quinonoid bromide, but which is now shown to be a compound of phenazthionium bromide, thiodiphenylamine, and hydrogen bromide,

$$C_6H_4\ll^{N}_{SBr}\gg C_6H_4,C_6H_4\lessdot^{NH}_{S}\gtrdot C_6H_4,HBr.$$

This substance is converted by sodium hydrogen sulphite into thiodiphenylamine and hydrogen bromide, and thus does not contain bromine in the nucleus; on preservation, however, bromination gradually occurs in the nucleus.

When a solution of thiodiphenylamine in ether is treated with excess of an ethereal solution of bromine, the olive-green precipitate which is first formed rapidly becomes pale brownish-red, *holo*quinonoid *phenazthionium perbromide*, $C_6H_4\ll^{N}_{SBr}\gg C_6H_4,Br_2$, being formed. This perbromide is probably a constituent of the compound obtained by Pummerer and Gassner at $-15°$ in alcoholic solution (which they describe as composed of 1 mol. *holo*quinonoid bromide + 1HBr).

The product of the action of iodine on thiodiphenylamine dissolved in chloroform probably has the composition,

$$C_6H_4\ll^{N}_{SI}\gg C_6H_4,I_2,C_6H_4\lessdot^{NH}_{S}\gtrdot C_6H_4,HI.$$

holo-Quinonoid phenazthionium perchlorate is anhydrous, whereas Pummerer and Gassner give $+1H_2O$. The *meri*-quinonoid perchlorate, $C_6H_4\ll^{N}_{S(ClO_4)}\gg C_6H_4,C_6H_4\lessdot^{NH}_{S}\gtrdot C_6H_4,HClO_4$, is also anhydrous.

holo-Quinonoid phenazthionium picrate,

$$N\ll^{C_6H_4}_{C_6H_4}\gg S\cdot O\cdot C_6H_2(NO_2)_3,$$

forms black needles. The reddish-brown and green phenazthionium picrates of Pummerer and Gassner have been re-investigated and appear to be half-quinonoid instead of *holo*-quinonoid.

Phenazthionium hydrogen sulphate is obtained by addition of thiodiphenylamine to cold concentrated sulphuric acid; when crystallised from boiling glacial acetic acid, it yields the normal *sulphate*. Both salts are half-quinonoid. *holo*-Quinonoid phenazthionium sulphate could only be obtained in solution. The *holo*-quinonoid nitrate could not be isolated, but a half-quinonoid salt, $C_{24}H_{18}O_6N_4S_2$, has been obtained in dark green crystals.

holo-Quinonoid 3 : 6-*dimethylphenazthionium perchlorate*, brownish-red needles, is prepared by the action of perchloric acid on the corresponding sulphoxide. The previously described chloride (A., 1906, i, 306) is now shown to be half quinonoid.

3-*Methoxythiodiphenylaminesulphoxide*, m. p. 198°, is obtained by the action of hydrogen peroxide on a saturated solution of methoxythiodiphenylamine in alcohol. With perchloric acid it yields a *holo*-quinonoid perchlorate, chocolate-brown crystals. The corresponding half-quinonoid salt has been described by Pummerer and

Gassner; when a solution of the latter is boiled, the methoxyl group is readily displaced, phenazthione being formed. H. W.

Some Thiazoles and Oxazoles. MARCEL BACHSTEZ (*Ber.*, 1914, **47**, 3163—3169).—Gabriel (A., 1910, i, 190, 431) and Rüdenberg (A., 1914, i, 52) have shown that when acylated α-aminoketones of the type $R{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}R'$, are heated with phosphorus pentasulphide or pentachloride they are converted into thiazoles or oxazoles, $R{\cdot}C\begin{matrix}N{-}CH\\ S(\text{or } O)\end{matrix}CR'$. The author has now prepared some compounds of this type in which the one alkyl or aryl radicle is replaced by hydrogen or the hydrogen atom of the CH-group is replaced by alkyl.

Benzoylaminoacetal, $NHBz{\cdot}CH_2{\cdot}CH(OEt)_2$, on warming with phosphorus pentasulphide, yielded 2-phenylthiazole (Hubacher, A., 1891, i, 220), but did not condense to the oxazole under the influence of the pentachloride or of sulphuric acid.

ω-Formylaminoacetophenone, m. p. 81—82° (Pictet and Gams, A., 1910, i, 774, gave m. p. 70—71°), was warmed with phosphorus pentasulphide, then treated with hydrochloric acid, filtered, rendered alkaline and distilled in steam, when *5-phenylthiazole* was obtained, in iridescent leaflets, m. p. 45—46°, with a peculiar fungoid odour (*hydrochloride*, hygroscopic, *platinichloride*, decomp. 281—282°, *aurichloride*, m. p. 185°, *dichromate*, m. p. 108—109° [decomp.], *picrate*, pale yellow, long needles, m. p. 138—139° [decomp.]). In the same way, using the pentachloride, *5-phenyloxazole* was obtained, m. p. 42° (*aurichloride*, m. p. 149—150°, *platinichloride*, stable at 275°).

Phthalyl-α-alanine ester was hydrolysed by warm concentrated sulphuric acid, then converted into α-aminopropiophenone (Gabriel, A., 1908, i, 181), and this was acetylated by means of acetic anhydride in the presence of cold sodium hydrogen carbonate solution. *α-Acetylaminopropiophenone*, $CH_3{\cdot}CHBz{\cdot}NHAc$, forms blunt, rhombic pyramids, m. p. 90—91°, and yields *5-phenyl-2 : 4-dimethyloxazole*, m. p. 51—52° (*hydrochloride*, hygroscopic, *chromate*, m. p. 100—101°, *platinichloride*, with $2H_2O$, m. p. 240°, *picrate*, m. p. 171—172·5°) and *5-phenyl-2 : 4-dimethylthiazole*, b. p. 270—271°/755 mm. (*hydrochloride*, hygroscopic, *platinichloride*, with $2H_2O$, m. p. 239—240°, *aurichloride*, *chromate*, m. p. 105—106°, *picrate*, m. p. 155·5—156·5°).

Benzoylaminoisobutyrophenone, $C_6H_5{\cdot}CO{\cdot}CMe_2{\cdot}NHBz$, was obtained by benzoylating the hydrochloride of the base (Gabriel, A., 1911, i, 212), and crystallises in long needles, m. p. 61°. It did not undergo condensation under the above conditions.

The hydrochloride of α-aminoacetophenone was also treated with ethyl oxalyl chloride, but the yield of *ω-ethoxalylaminoacetophenone*, $CH_2Bz{\cdot}NH{\cdot}CO{\cdot}CO_2Et$, long prisms, m. p. 96—97°, was so small that further condensations were impossible. J. C. W.

A Preparation of Thiazole. S. GABRIEL and MARCEL BACHSTEZ (*Ber.*, 1914, **47**, 3169—3171).—The simplest thiazole could be obtained by the condensation of formylaminoacetaldehyde by means of

phosphorus pentasulphide (compare preceding abstract). As this appears to be a very elusive substance, however, the corresponding acetal has been investigated.

Ethyl formate and aminoacetal were warmed in a sealed tube and thus converted into *formylaminoacetal*, $H{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH(OEt)_2$, a colourless, viscous oil, b. p. 141—142°/14 mm., and an intimate mixture of this with phosphorus pentasulphide was heated at 160°, and the steam distillate of the resultant base was precipitated by mercuric chloride. The yield of thiazole, calculated on the weight of the mercuric chloride compound (Popp. A., 1889, 724), was 62%.

J. C. W.

Autoxidation of Hydrazones. M. Busch and Wilhelm Dietz (*Ber.*, 1914, **47**, 3277—3291).—The action of air and light on alcoholic solutions of aldehydephenylhydrazones has been investigated by Stobbe and Nowak (A., 1913, i, 1200), who found that the change was not due, as supposed by Baly and Tuck (T., 1907, **91**, 1572), to photo-isomerisation of the hydrazones to azo-compounds, but to an oxidation process whereby hydrotetrazones, aldehydes, acids and resinous matters are formed. The authors find the action to follow a different course when solutions of hydrazones in hydrocarbons are employed, and that the primary product is a peroxide which, under suitable circumstances, can be readily isolated. These peroxides are relatively stable in solution, but, when dry, are generally highly unstable, frequently exploding after a short time without apparent reason. Benzaldehyde-*p*-bromophenylhydrazone in this respect forms a marked exception to the general rule.

The peroxides have the general formula $\begin{matrix} R{\cdot}CH{\cdot}N{\cdot}NH{\cdot}R \\ | \quad | \\ O{-}{-}O \end{matrix}$, since substances closely similar both in preparation and properties are obtained by the autoxidation of hydrazones from asymmetric secondary hydrazines and of ketohydrazones; hence, the two labile hydrogen atoms of aldehyde-hydrazones do not play a part in the formation of peroxides, and thus there is only one possible mode of addition of the oxygen molecule. Water does not appear to have a marked effect on the autoxidation of hydrazones.

In conformity with Engler's observations, the hydrazone peroxides readily give up one atom of oxygen, and can thus be estimated iodometrically, one half of the oxygen being used in oxidising the hydriodic acid, whilst the other remains in the molecule, forming the corresponding acyl hydrazine:

$$\begin{matrix} R{\cdot}CH{\cdot}N{\cdot}NHR \\ | \quad | \\ O{-}{-}O \end{matrix} + 2HI = I_2 + H_2O + R{\cdot}C(OH){:}N{\cdot}NHR \longrightarrow R{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}R.$$

The hydrazone peroxides are very susceptible to the action of hydrogen and hydroxyl ions. In the former case an acylhydrazine is first formed, which is partly oxidised by the available oxygen atom of the unchanged peroxide to the corresponding azo-compound; in the latter case, larger quantities of other products are formed, benzaldehydephenylhydrazone, for example, giving nitrogen, oxygen, benzene, benzaldehyde,

and benzoic acid. The primary action probably occurs according to the equation: $\mathrm{Ph\cdot\overset{O}{\overset{|}{C}}H\cdot\overset{O}{\overset{|}{N}}\cdot NHPh} = \mathrm{Ph\cdot CHO + N_2 + O + C_6H_6}$.

Small quantities of hydrogen peroxide are formed by the decomposition of the peroxides by dilute sulphuric acid.

Peroxides of two ketohydrazones have been investigated by Freer (A., 1899, i, 357), who assumed them to be azo-compounds.

The preparation of the peroxides is generally effected by the action of oxygen under slight pressure on a solution or suspension of the requisite hydrazone in benzene or petroleum.

Benzaldehydephenylhydrazone peroxide forms canary-yellow needles, m. p. 65—66° (decomp.). It becomes brown on exposure to light, and, when dry, usually explodes within a few minutes, even when shielded from light and placed in a vacuum. At temperatures below 0°, it is rather more stable. Concentrated sulphuric or nitric acid causes it to explode; alcoholic hydrogen chloride acts on it in ethereal solution, yielding benzoylphenylhydrazine, m. p. 168°, and benzoylazobenzene. When dissolved in alcohol and treated with aqueous ammonia, it gives benzaldehyde, benzoylphenylhydrazine, benzoic acid, and benzene. Catalytic reduction of benzaldehydephenylhydrazone peroxide by palladianised calcium carbonate requires the calculated quantity of hydrogen and gives an almost quantitative yield of the hydrazone.

Benzaldehyde-p-*tolylhydrazone peroxide* forms sulphur-yellow needles, m. p. 77—78° (decomp.). Exclusion of moisture during oxidation does not appear to affect the process in any way.

Benzaldehyde-p-*bromophenylhydrazone peroxide* forms sulphur-yellow prisms or leaflets, m. p. 107—108° (decomp.), and can be preserved unchanged for months if protected from light. Measurements of absorption of oxygen by the hydrazone show that the process cannot be made absolutely quantitative.

Benzaldehyde-p-*chlorophenylhydrazone peroxide*, yellow needles, m. p. 104—105°, resembles the *p*-bromo-compound in stability.

Anisaldehydephenylhydrazone peroxide, shining, yellow needles, decomposes at 83—84°.

m-*Nitrobenzaldehydephenylhydrazone peroxide*, yellow needles, decomposes at 83—84°. Addition of oxygen is rendered difficult if a nitro-group is present in the nucleus of the aryl hydrazine; benzaldehyde-*o*-nitrophenylhydrazone does not absorb oxygen, whilst the corresponding meta- and para-derivatives only react very slowly. A similar difficulty is experienced with cinnamaldehydephenylhydrazone.

Benzaldehydephenylbenzylhydrazone absorbs oxygen fairly readily, yielding the corresponding *peroxide*, lemon-yellow needles, which decompose at 70—71°. Acetone-*p*-bromophenylhydrazone reacts very readily with oxygen. The *peroxide* formed, yellow leaflets, m. p. 45—47° (decomp.), appears to be identical with the product described by Freer (*loc. cit.*).

Acetophenone-*p*-bromophenylhydrazone peroxide (compare Freer, *loc. cit.*) forms canary-yellow needles, m. p. 48—49°. H. W.

Action of Zinc Hydroxide and Ammonia on Rhamnose. Adolf Windaus and Arthur Ullrich (*Zeitsch. physiol. Chem.*, 1914, **92**, 276—285. Compare A. 1907, i, 288).—A mixture of rhamnose,

zinc hydroxide, and ammonia after remaining at the ordinary temperature for one year deposits a quantity of zinc salts from which, by treatment with hydrogen sulphide followed by extraction with ether and precipitation with ethereal oxalic acid, 4-methylglyoxaline oxalate, m. p. 205°, is obtained. The free base is identical with that obtained in a similar way from dextrose.

The substances remaining in the ethereal solution after the removal of the precipitated 4-methylglyoxaline oxalate are separated by the fractional crystallisation from water of their picrates. The most soluble picrate (m. p. 159—160°) is that of the above 4-methylglyoxaline. The largest fraction of medium solubility consists of 2 : 4-dimethylglyoxaline picrate, m. p. 141—142°. The free base has m. p. 92°, and is identical with the synthetic product (Windaus, A., 1907, i, 90). The *picrolonate* crystallises in rosettes of minute needles, m. p. 263° (decomp.). The least soluble picrate was obtained after many recrystallisations in the form of long, lemon-yellow needles, m. p. 154°. Comparison with the picrates of 2 : 4 : 5-trimethylglyoxaline and of 4-ethylglyoxaline, prepared by reduction of 4-β-hydroxyethylglyoxaline (A., 1911, i, 752) with hydriodic acid, showed that it differed from either of these compounds. It is therefore probably the *picrate*, $C_{12}H_{13}O_7N_5$, of the base, *2-methyl-4-ethylglyoxaline*, $C_6H_{10}N_2$.

From the mother liquor after removal of the deposited zinc salts, two compounds of undetermined composition have been isolated. The analysis of one of these gives the formula C_6H_7ON, colourless prisms from methyl alcohol, m. p. 120° with loss of water; the other compound, $C_8H_{11}O_2N$, crystallises from a mixture of alcohol and ether in needles, m. p. above 300°, and sublimes in a vacuum at this temperature. It appears to be a derivative of dihydroxypyridine, and gives with ferric chloride, even in very dilute solution, a characteristic colour reaction which is at first red, then blue, and eventually green.

H. W. B.

Constitution of the Blood Pigments; Dipyrrylmethane Derivatives with Structure of Dyes. Hans Fischer (*Ber.*, 1914, **47**, 3266—3277).—The first part of this paper is mainly polemical against Piloty (A., 1914, i, 327, 755); in the second part, further experiments on the condensation of glyoxal with pyrroles are described (compare A., 1914, i, 994).

[With Miss Johanna Baümer.]—*Di*(2 : 4-*dimethylpyrryl*)*methane hydriodide*, red needles, m. p. 283°, is obtained by the addition of hydriodic acid to the product of the action of 2 : 4-dimethylpyrrole on an alcoholic solution of glyoxal. Attempts to isolate the *hydrochloride* gave less satisfactory results. The free *base*, pale yellow plates, has m. p. 118—119°. The *picrate*, brown plates with bluish glance, decomposes at 215°. A methyl-alcoholic solution of potassium methoxide converts the hydrochloride into tetramethylpyrrole, m. p. 105—106° (picrate, m. p. 128°). Reduction with a solution of hydriodic acid in glacial acetic acid transforms the hydriodide into 2 : 4-dimethylpyrrole (identified as the picrate, m. p. 93—94°). Citraconimide, m. p. 226—228°, is formed by the action of nitrous acid on the free base.

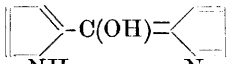
[With KARL EISMAYER.]—The condensation of 3-acetyl-2 : 4-dimethylpyrrole with glyoxal and hydrochloric acid has been studied previously (A., 1914, i, 994), and a product has been isolated, m. p. 225°, which has been considered to be a hydrochloride of *s*-tetra(3-acetyl-2 : 4-dimethylpyrryl)ethane. This product is obtained when the reaction mixture is heated for two minutes; when heated for a shorter time, however, a different *product*, thick, prismatic rods which soon become yellowish-red on exposure to light and decompose at 185°, is produced. This has a higher chlorine content than the former, but does not appear to be uniform. The two products are closely related, since, on reduction, each gives the same substance; the direct conversion of the one into the other has not been effected. Boiling ammonia or pyridine does not completely remove chlorine from the substance, m. p. 185°.

Hydrogen chloride can be eliminated from either of the above substances by means of a boiling solution of sodium acetate in glacial acetic acid. The *product* so obtained forms thick prisms, m. p. 268°, which rapidly become reddish-brown on exposure to air, are extremely hygroscopic, and very sensitive to light. Analyses lead to a formula, $C_{34}H_{40}O_4N_4$, but the authors are unable to suggest a constitution. The substance is not identical with Colacicchi's bis-3-acetyl-2 : 4-dimethylpyrrylmethane (A., 1911, i, 1030), or with the product described by Piloty (*Ber.*, 1914, **47**, 2542).

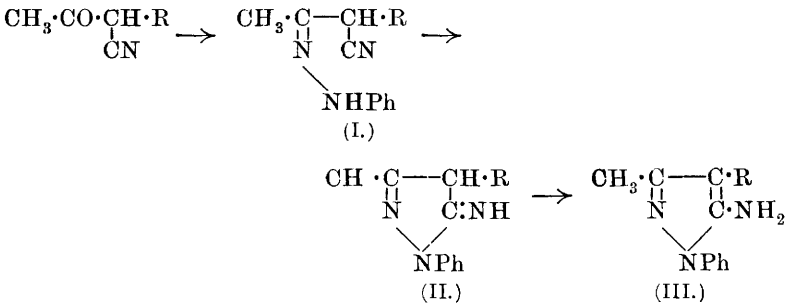
Reduction of the products, m. p. 225° and 185° respectively, with glacial acetic–hydriodic acid yields a small quantity of dimethylpyrrole and a *substance*, $C_{17}H_{22}O_2N_2$, leaflets, m. p. 296—297°, the constitution of which has not been elucidated. Determination of molecular weight in glacial acetic acid gave the value 269, whilst on treatment with potassium methoxide at 220°, tetramethylpyrrole is formed.

Further investigation of the substance, m. p. 225°, shows that the previously adopted constitution [hydrochloride of *s*-tetra(3-acetyl-2 : 4-dimethylpyrryl)methane] is probably incorrect. Chlorine cannot be completely removed by sodium hydroxide, alcoholic ammonia, or pyridine; possibly the substance is chlorotetra(3-acetyl-2 : 4-dimethylpyrryl)ethane. H. W.

Methods of Preparation of Di-2-pyrryl Ketone. V. V. TSCHELINCEV and D. K. SKVORCOV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 170—176).—Ciamician and Magnaghi's method for preparing di-2-pyrryl ketone from potassiopyrrole and carbonyl chloride (A., 1885, 809) gives a very poor yield. Better results are obtained by the action of magnesium 2-pyrryl chloride and the chloro-anhydride of pyrrole-2-carboxylic acid (compare Fischer and van Slyke, A., 1911, i, 1020), and still better by the interaction of magnesium 2-pyrryl chloride and carbonyl chloride, this reaction giving a yield of 28·5%. The indifference of this ketone to hydroxylamine and semicarbazide and its solubility in hydrochloric acid indicate that it exhibits a marked tendency to undergo transformation into the pseudo-enolic modification (annexed formula). It is a highly stable compound and undergoes condensation processes only with difficulty. T. H. P.



5-Amino-4-alkylpyrazoles. Ernst Mohr (*J. pr. Chem.*, 1914, [ii], **90**, 223—256).—The α-cyano-ketones (monoalkylacetoacetonitriles) (this vol., i, 221) give unstable phenylhydrazones, which by warming for a short time with dilute hydrochloric acid are isomerised into 5-amino-1-phenyl-3-methyl-4-alkylpyrazoles (III).



The phenylhydrazones (I) are well crystalline, almost white substances, which decompose after a few hours' exposure to the air. Their reducing action on Fehling's solution, the odour of cyano ketone often noticed on boiling them with hydrochloric acid, and their similarity in many respects to cyanoacetonephenylhydrazone afford evidence for regarding them as true phenylhydrazones, in spite of Bouveault's statement that only α-dialkylcyanoketones yield phenylhydrazones (A., 1891, i, 51), whilst the fact that the phenylbenzylhydrazone of ethylacetoacetonitrile did not condense to an aminopyrazole, but was split into its components on boiling with hydrochloric acid, speaks for the correctness of the above conception of the isomerisation, since the requisite hydrogen atom in the phenylhydrazine residue is absent in this case.

The identity of some of the aminopyrazoles with those obtained by Michaelis (A., 1901, i, 407; 1905, i, 476) from pyrazolones proves that the alkylation of diacetonitrile proceeds in the same way as that of acetoacetic ester, the alkyl group attaching itself to the α-carbon atom.

5-Amino-1-phenyl-3 : 4-dimethylpyrazole, $NPh\langle\begin{matrix}N{=}CMe\\ C(NH_2)\end{matrix}\rangle CMe$, was prepared by warming the phenylhydrazone of methylacetoacetonitrile (which could not be isolated in a pure state owing to the ease with which isomerisation occurred) with hydrochloric acid until a clear solution was obtained, and precipitating the base with sodium hydroxide. It forms a colourless, crystalline mass, m. p. 105—106°, b. p. 206·5°/20 mm., or 336—338°/753 mm. without decomposition. It is very stable towards boiling acids and alkalis, and gives with concentrated sulphuric acid and sodium nitrite an intense yellow liquid which on diluting and warming becomes blood-red. The following derivatives are described: Hydrochloride,

$$C_{11}H_{13}N_3,HCl,\tfrac{1}{2}H_2O,$$

forming long needles, m. p. 70—71°, or 155° when anhydrous; platinichloride, m. p. 192—193°; sulphate, needles, m. p. 190°; picrate,

m. p. 137°; *benzoyl* derivative, m. p. 196°; *benzylidene* derivative, yellow needles, m. p. 88°.

Ethylacetoacetonitrilephenylbenzylhydrazone, prepared by heating the constituents in alcoholic solution for two hours, forms a white, crystalline powder, m. p. 96°, which with hydrochloric acid yields no pyrazole derivative.

Ethylacetoacetonitrilephenylhydrazone, bright yellow prisms, m. p. 73—74°, is unstable in the air.

5-*Amino*-1-*phenyl*-3-*methyl*-4-*ethylpyrazole*, $C_3N_2MeEtPh\cdot NH_2$, prepared in the same manner as the methyl homologue, or direct from ethylacetoacetonitrile without isolating the phenylhydrazone, forms colourless prisms or rhombic tablets, m. p. 53°, b. p. 198°/15 mm., or 341—343°/763 mm. It forms with benzene a *compound*, $6C_{12}H_{15}N_3 + C_6H_6$, and gives the colour reaction with sulphuric acid and sodium nitrite. The *hydrochloride* melts at 194—195°, and the *benzoyl* derivative at 233°. An *argentonitrate* is also described.

n-*Propylacetoacetonitrilephenylhydrazone*, snow-white prisms, m. p. 64°, rapidly resinifies on keeping.

5-*Amino*-1-*phenyl*-3-*methyl*-4-n-*propylpyrazole*, $C_3N_2MePrPh\cdot NH_2$, forms a leafy, crystalline mass, m. p. 55°. Its *hydrochloride* melts at 207°, and *benzoyl* derivative at 150°.

Allylacetoacetonitrilephenylhydrazone likewise forms extremely unstable, white prisms, m. p. 60°.

Benzylacetoacetonitrilephenylhydrazone forms pale yellow needles, m. p. 112°. It is also unstable, becoming in two days a dark resinous mass.

5-Amino-1-phenyl-4-benzyl-3-methylpyrazole,

$$NH_2\cdot C_3N_2MePh\cdot CH_2Ph,$$

prepared by the action of hydrochloric acid or sodium hydroxide on the isomeric phenylhydrazone, is an oily liquid which slowly sets to a crystalline solid, m. p. 76°, b. p. 259—260°/13 mm. Like some of its homologues, it dissolves in excess of the precipitant if liberated from its hydrochloride by very dilute alkali, but it is insoluble in concentrated alkali hydroxides. The hydrochloride, m. p. 189°, is considerably hydrolysed by water, the base being partly precipitated as an oil. An *argentonitrate*, $C_{17}H_{17}N_3,AgNO_3$, and a benzoyl derivative, m. p. 178° (Michaelis and Preuner give 184°, *loc. cit.*), are also described.

G. F. M.

4-Amino-1-phenyl-3-methylpyrazole and the Semidine Transformation in the Pyrazole Series. A. Michaelis and Arthur Schäfer (*Annalen*, 1915, **407**, 229—274).—5-Chloro-4-amino-1-phenyl-3-methylpyrazole (following abstract) is reduced by 20% hydriodic acid and amorphous phosphorus at a temperature not exceeding 150—160°, and yields 4-*amino*-1-*phenyl*-3-*methylpyrazole*,

$$NPh\begin{cases} N{=}CMe \\ CH{:}C\cdot NH_2 \end{cases},$$

colourless needles, m. p. 88°, b. p. 312—313° (*hydrochloride*, colourless needles or leaflets, m. p. 209°; *platinichloride*, yellow needles, m. p. 226° [decomp.]; *picrate*, yellow needles, m. p. 138° [decomp.]). In its salts, its behaviour with acid chlorides, and in the formation of a

carbamide, the base is quite analogous to the 5-amino-isomeride (A., 1907, i, 735), but in other respects the two compounds are very dissimilar; for example, 4-amino-1-phenyl-3-methylpyrazole is readily diazotised, condenses with aldehydes at the ordinary temperature, and in hydrochloric acid reacts with bromine water, thereby losing its amino-group and yielding a *substance*, colourless needles, m. p. 168°, reddening at 72°, which exhibits the properties of a brominated 5-pyrazolone.

By careful oxidation in glacial acetic acid by 3% hydrogen peroxide, 4-amino-1-phenyl-3-methylpyrazole yields *4-amino-?:?-dihydroxy-1-phenyl-3-methylpyrazole*, $C_{10}H_{11}O_2N_3$, reddish-yellow or orange needles, m. p. 187°. The constitution of this substance is being examined. It may be an oximino-compound, because it is converted by hot concentrated hydrochloric acid into 4-oximino-1-phenyl-3-methyl-5-pyrazolone, 4-azo-1-phenyl-3-methylpyrazole (see below), and 4-amino-1-phenyl-3-methylpyrazole; also, it is reduced to the last substance by alcohol and an excess of aqueous sodium hydroxide.

The following 4-arylideneamino-derivatives have been prepared from 4-amino-1-phenyl-3-methylpyrazole and the requisite aldehyde, either by heating the two substances or by their reaction in glacial acetic acid; *benzylidene* derivative, $CHPh:N\cdot C\begin{cases}CH{-}{-}NPh\\ CMe{:}N\end{cases}$, colourless crystals, m. p. 113°; p-*nitrobenzylidene* derivative, orange-yellow needles, m. p. 169°; *salicylidene* derivative, yellow needles, m. p. 103°; and p-*methoxybenzylidene* derivative, colourless leaflets, m. p. 101°.

4-Amino-1-phenyl-3-methylpyrazole reacts (*a*) with thionyl chloride in hot benzene to form *4-thionylamino-1-phenyl-3-methylpyrazole*, $SO:N\cdot C\begin{cases}CH{-}{-}NPh\\ CMe{:}N\end{cases}$, yellow leaflets, m. p. 55—56°, (*b*) with anhydrous formic acid on the water-bath to form *4-formylamino-1-phenyl-3-methylpyrazole*, slender needles containing $1H_2O$, m. p. 71—81°, (anhydrous) 112—113°, and (*c*) with acetic anhydride and with benzoyl chloride to form the *4-acetylamino*-derivative, colourless needles containing $1H_2O$, m. p. 94—95°, or anhydrous prisms, m. p. 120°, and the *4-benzoylamino*-derivative, colourless needles, m. p. 181°, respectively. The *carbamide*, $C_{11}H_{12}ON_3$, colourless needles, m. p. 198°, *phenylcarbamide*, $C_{10}N_2H_9\cdot NH\cdot CO\cdot NHPh$, m. p. 193°, and *phenylthiocarbamide*, m. p. 173°, are obtained by the usual methods, whilst 4-amino-1-phenyl-3-methylpyrazole and carbon disulphide at 150° yield *s-1-phenyl-3-methyl-4-pyrazolylthiocarbamide*, $CS(NH\cdot C_{10}H_9N_2)_2$, m. p. 189°.

4-Amino-1-phenyl-3-methylpyrazole is readily diazotised at the ordinary temperature. The *diazonium chloride*, $C_{10}H_9N_4Cl$, colourless, hygroscopic leaflets, m. p. 101° (decomp.), does not explode by heating or percussion, does not lose nitrogen even in a boiling acid solution, and reacts with β-naphthol in alkaline solution to form *1-phenyl-3-methylpyrazole-4-azo-β-naphthol*, $C_{20}H_{16}ON_4$, red needles, m. p. 189°, and with 1-phenyl-3-methyl-5-pyrazolone in glacial acetic acid to form *1-phenyl-3-methylpyrazole-4-azo-1-phenyl-3-methyl-5-pyrazolone*,

$$\begin{matrix}NPh\cdot CH\\ N{:}CMe\end{matrix}\!\!>C\cdot N_2\cdot CH<\begin{matrix}CO{-}{-}NPh\\ CMe{:}N\end{matrix},$$

red needles, m. p. 220° (decomp.). 5-*Chloro*-4(4′)-*azo*-1-*phenyl*-3-*methylpyrazole*, $C_{10}H_8N_2Cl\cdot N_2\cdot C_{10}H_9N_2$, yellow leaflets, m. p. 157°, prepared from the last compound and phosphoryl chloride at 150°, is converted into 4-amino-1-phenyl-3-methylpyrazole by hydriodic acid and amorphous phosphorus, and is reduced by zinc dust and sodium hydroxide in boiling aqueous alcoholic solution to 4-*hydrazo*-1-*phenyl*-3-*methylpyrazole*, $C_{20}H_{20}N_6$, almost colourless leaflets or needles, m. p. 209°. 4-*Azo*-1-*phenyl*-3-*methylpyrazole*, $C_{20}H_{18}N_6$, yellow needles, m. p. 259—260°, is obtained in about 10% yield by heating 5-chloro-4-amino-1-phenyl-3-methylpyrazole with equal parts of alcohol and ether at 150° (Michaelis and Bressel, following abstract). It can also be obtained by oxidising the hydrazo-compound with hydrogen peroxide and glacial acetic acid, but is best prepared by heating 4-aminoantipyrine chloride (Michaelis and Stan, A., 1914, i, 93) with alcohol and ether at 150°. The azopyrazole distils almost without decomposition, exhibits a yellowish-green fluorescence in electric light or in ethereal solution, and is insoluble in acids. It is reduced to 4-amino-1-phenyl-3-methylpyrazole by hydriodic acid (D 1·7), amorphous phosphorus, and glacial acetic acid at 150—160°, but the process is untrustworthy. In hot glacial acetic acid the azopyrazole is converted by chlorine and by bromine into 4-*azo*-1-*chlorophenyl*-3-*methylpyrazole*, $C_{20}H_{16}N_6Cl_2$, yellow needles, m. p. 325°, and the corresponding *bromo*-compound, yellow needles, m. p. 352°, respectively, both of which are very stable substances. 1-Phenyl-3-methylpyrazole-4-azobenzene (Michaelis and Leonhardt, A., 1905, *i*, 392) is best obtained in quantity by heating Knorr's 1-phenyl-3-methyl-5-pyrazolone-4-azobenzene with phosphoryl chloride at 140°, and reducing the resulting 5-chloro-compound by Michaelis and Leonhardt's method (*loc. cit.*).

By reducing 1-phenyl-3-methylpyrazole-4-azobenzene in alcoholic solution with stannous chloride and hydrochloric acid, Abraham (*Diss.*, Rostock, 1909) obtained a substance, m. p. 141°, to which he assigned the formula $C_{10}H_{11}N_3$. It has now been found that the formula is

$$C_{16}H_{16}N_4,$$

and that the substance is 4-amino-5-anilino-1-phenyl-3-methylpyrazole (Michaelis and Reese, A., 1911, *i*, 1037), which has been formed from the phenylmethylpyrazoleazobenzene by a semidine transformation of the intermediately formed hydrazo-compound.

A purer product is obtained when sodium hyposulphite is the reducing agent. However, when 1-phenyl-3-methylpyrazole-4-azobenzene is reduced by stannous chloride and concentrated hydrochloric acid in the absence of alcohol, the product is an isomeric *substance*,

$$C_{16}H_{16}N_4,$$

colourless needles or leaflets, m. p. 188—189°, which appears to be 4-*aminoanilino*-1-*phenyl*-3-*methylpyrazole*,

$$NH_2\cdot C_6H_4\cdot NH\cdot C\begin{matrix}=CH-NPh\\ \quad\quad |\\ -CMe{:}N\end{matrix}$$

It forms an easily soluble *hydrochloride*, needles or prisms, m. p. 292° (decomp.), and *acetyl* derivative, colourless needles containing $2\frac{1}{2}H_2O$, m. p. 149° (decomp.), 239° (anhydrous), and is readily diazotised, the very stable diazonium salt reacting with β-naphthol in alkaline solution to form a red *azo*-compound, m. p. 263—264°.

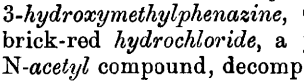
The two isomerides, $C_{16}H_{16}N_4$, are quite analogous to the two compounds $C_{15}H_{14}N_4$, m. p. 95—97° and 192—193° respectively, obtained by Zincke and Kegel in 1889 by the reduction of 1-phenylpyrazole-4-azobenzene by stannous chloride and hydrochloric acid; the constitutions of the latter pair, which have not been investigated since their discovery, doubtless correspond with those ascribed above to the former pair.

In addition to the derivatives already recorded (*loc. cit.*), 4-amino-5-anilino-1-phenyl-3-methylpyrazole forms a *hydriodide*, slender needles, *sulphate*, $2C_{16}H_{16}N_4,H_2SO_4$, m. p. 220° (decomp.), *acetyl* derivative, m. p. 134° (hydrated) or 162° (anhydrous), *benzoyl* derivative, m. p. 187°, and *carbamide*, m. p. 201°, and condenses with aldehydes to form the following 4-arylideneamino-derivatives: *benzylidene* derivative, faintly yellow crystals, m. p. 148°, *salicylidene* derivative, yellow prisms, m. p. 147°, p-*methoxybenzylidene* derivative, faintly yellow leaflets, m. p. 194°; it also reacts with warm ethyl acetoacetate to form the *compound* $C_{16}H_{14}N_3\cdot N{:}CMe\cdot CH_2\cdot CO_2Et$, colourless needles, m. p. 127°. C. S.

5-Chloro-4-amino-1-phenyl-3-methylpyrazole and its Derivatives. A. Michaelis and Hans Bressel (*Annalen*, 1915, **407**, 274—289).—An improved method of reducing 5-chloro-1-phenyl-3-methylpyrazole-4-azobenzene or -4-azo-*p*-toluene (A., 1904, i, 940; 1905, i, 392) is the heating of the azo-compound on the water-bath with tin and saturated alcoholic hydrogen chloride; on cooling, 5-chloro-4-amino-1-phenyl-3-methylpyrazole hydrochloride (m. p. 227°, not 220°; *loc. cit.*) crystallises.

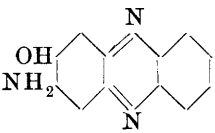
The base distils without decomposition under reduced pressure and in general behaves like 4-amino-1-phenyl-3-methylpyrazole (preceding abstract). It forms a *platinichloride*, $2C_{10}H_{10}N_3Cl,H_2PtCl_6$, golden-yellow crystals, m. p. above 280° (decomp.), *picrate*, yellow crystals, m. p. 95°, *formyl* derivative, colourless leaflets, m. p. 137°, *benzoyl* derivative, m. p. 148°, *acetyl* derivative, m. p. 123°, *benzenesulphonyl* derivative, colourless prisms, m. p. 154°, *carbamide*, $C_{11}H_{11}ON_4Cl$, m. p. 230°, *phenylcarbamide*, m. p. 216°, and *phenylthiocarbamide*, m. p. 182°, reacts with methyl iodide to form 5-chloro-4-dimethylamino-1-phenyl-3-methylpyrazole hydriodide, and condenses with aromatic aldehydes to form 4-arylideneamino-derivatives; the *benzylidene* derivative, faintly yellow needles, m. p. 72°, p-*nitrobenzylidene* derivative, intensely yellow needles, m. p. 141°, *salicylidene* derivative, yellow leaflets, m. p. 100°, and p-*methoxybenzylidene* derivative, almost colourless needles, m. p. 91—92°, and also the 4-*thionylamino*-derivative, $C_{10}H_8ON_3S$, faintly yellow prisms, m. p. 128°, have been prepared.

5-Chloro-4-amino-1-phenyl-3-methylpyrazole is readily diazotised. The resulting solution, which can be boiled without decomposition occurring, yields with an alkaline solution of β-naphthol, 5-*chloro*-1-*phenyl*-3-*methylpyrazole*-4-*azo*-β-*naphthol*, red needles, m. p. 199°, and with 1-phenyl-3-methyl-5-pyrazolone in glacial acetic acid, 5-*chloro*-1-*phenyl*-3-*methylpyrazole*-4-*azo*-1-*phenyl*-3-*methyl*-5-*pyrazolone*, red needles, m. p. 143°. By heating the latter with phosphoryl chloride at 140°, 5:5′-*dichloro*-4(4′)-*azo*-1-*phenyl*-3-*methylpyrazole*, yellow

needles, m. p. 226°, is obtained. This substance is more conveniently prepared as follows. By the reaction between diazotised antipyrine and 1-phenyl-3-methyl-5-pyrazolone in glacial acetic acid, Knorr and Stolz in 1896 obtained a substance which they called the antipyrylhydrazone of 1-phenyl-3-methylpyrazole-4 : 5-dione. The authors regard it as an azo-compound (annexed formula). In accordance with this view, the compound is converted by phosphoryl chloride at 150° into 5 : 5′-*dichloro*-4 : 4′-*azo*-1-*phenyl*-3-*methylpyrazole* 2-*methochloride*,  , yellow leaflets containing $1H_2O$, m. p. 220°, from which the azopyrazole is obtained by heating.

C. S.

Synthesis of 2-Amino-3-hydroxyphenazine. F. KEHRMANN and DORA KISSINE (*Ber.*, 1914, **47**, 3100—3101).—Ullmann and Mauthner obtained 2-amino-3-hydroxyphenazine by the oxidation of *o*-phenylenediamine with ferric chloride (A., 1903, i, 199). It has now been synthesised by condensing *o*-phenylenediamine hydrochloride with aminohydroxy-*o*-benzoquinone (A., 1907, i, 447), which confirms the annexed formula.



The same condensation has been effected with tolylene-3 : 4-diamine. The resultant 2-*amino*-3-*hydroxymethylphenazine*, $C_{13}H_{11}ON_3$, is orange-yellow and forms a brick-red *hydrochloride*, a yellow *diacetyl* derivative, and a deep red N-*acetyl* compound, decomp. 250°.

J. C. W.

Colour and Constitution of the Monoamines Derived from Phenyl*iso*naphthaphenazonium. VI. Quinoneimide Dyes. F. KEHRMANN, R. SPEIBEL, and E. GRANDMOUGIN (*Ber.*, 1914, **47**, 3363—3369).—The authors have examined the seven known isomeric monoamines derived from phenyl*iso*naphthaphenazonium, each of which forms three series of salts.

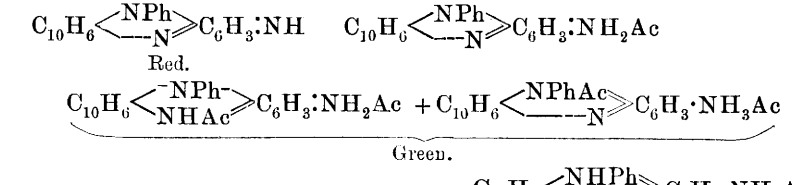
The first group comprises such amines as contain the NH_2 group in the benzenoid nucleus of the naphthalene. The di-acidic salts are orange-yellow, resembling the mono-acidic salts of the parent substance; the tri-acidic salts are brownish-red. On the other hand, the mono-acidic salts and the bases show marked differences; the former are yellowish-green in the case of the 6-amine, bluish-green (7-amine), and intensely violet (7-amine). The parent base and the 6- and 8-amines yield comparatively stable, lemon-yellow ψ-bases when treated with an excess of alkali, whereas the 7-amine gives a blue base, probably *amphi*-quinonoid in character, which passes into a greenish-yellow ψ-base. Spectroscopically, the mono-acidic salts of the parent substance and the di-acidic salts of the three amines behave identically. The di-acidic salts of the former and the tri-acidic salts of the latter give bands at $\lambda = 632$, 598 and 503$\mu\mu$ (for the parent substance), $\lambda = 586$, 539, 482$\mu\mu$ (6-amine), $\lambda = 583$, 535, 485$\mu\mu$ (7-amine), and $\lambda = 584$, 536, 482$\mu\mu$ (8-amine), thus

confirming the *ortho*-quinonoid formula. The mono-acidic salts of these amines show bands at corresponding points in the visible spectrum, although the subjective colours are markedly different; the result is possibly due to error of observation.

The second group contains the 2- and 9-amines which contain the amino-group in the para-position to the quinquevalent nitrogen atom. The di-acidic salts are green or blue; the tri-acidic salts are brownish-purple red (9-amine) and violet-brown (2-amine). Comparison of their spectra in both the visible and invisible region with those of the di-acidic salts of the parent substance indicates an ortho-quinonoid structure.

The colour changes observed during the conversion of the mono- into the di-acidic salts point to a para-quinonoid structure for these series; this, however, is not confirmed by spectroscopic determinations which indicate an ortho-quinonoid formula.

The 3-amine, which contains an amino-group in the para-position to the tervalent nitrogen atom of the azine nucleus, behaves somewhat differently. It gives a red imino-base, soluble in ether, the shade of which is somewhat yellower than that of the violet-red mono-acidic salt, a green di-acidic salt and a violet-brown, ortho-quinonoid tri-acidic salt (annexed formulæ).



Red.

Green.

Violet-brown.

The 10-amine gives a greenish-yellow mono-acidic, an orange-yellow di-acidic and a violet-brown tri-acidic salt as well as a lemon-yellow pseudo-base which is soluble in ether; it behaves, therefore, as an ortho-quinonoid amine of this class. Spectroscopic investigation is not yet completed. H. W.

Hydrazinedicarbamides. M. Busch and Hans Lotz (*J. pr. Chem.*, 1914, [ii], **90**, 257—273).—In continuation of the work on the internal condensation of hydrazinedithiocarbophenylamide (A., 1913, i, 907), the two simplest condensation products, viz., those from hydrazinedicarbothiamide, were prepared by Freund and Imgart's process, that is, by boiling with concentrated hydrochloric acid (A., 1895, i, 400). A mixture of the *hydrochloride of di-iminotetrahydrothiodiazole* and *iminodihydrothiodiazolethiol* was obtained and separated by crystallisation from water. The latter substance, designated by Freund and Imgart as dithiourazole, has, however, the constitution $\begin{matrix}NH\cdot C(NH)\\ |\\ N{=}{=}C(SH)\end{matrix}\!\!>S$, as is shown by its acid properties and by the formation of only a monobenzyl derivative (m. p. 157—158°), which no longer exhibits the properties of a mercaptan and cannot be oxidised to a disulphide. The basic substance obtained, as above

mentioned, as its hydrochloride has the constitution $\begin{matrix}NH\cdot C(NH)\\ |\\ NH\cdot C(NH)\end{matrix}\!\!>\!S$. The triazole formula ascribed to it by Freund is excluded because the substance does not also possess acidic properties, and its diacetyl derivative is not hydrolysed with the ease with which a *S*-acetyl group would be expected to react.

Hydrazinedicarbothiomethylamide, NHMe·CS·NH·NH·CS·NHMe, was prepared by the action of hydrazine hydrate on an alcoholic solution of methylthiocarbimide (2 mols.), first in the cold, and then warming until precipitation occurs. It crystallises from hot water in colourless, leafy crystals, m. p. 210°.

When boiled with hydrochloric acid, the following methyl compounds analogous to the above-described substances were obtained. *Methylaminothiodiazolethiol*, $\begin{matrix}N{:}C(NHMe)\\ |\\ N{=}{=}C(SH)\end{matrix}\!\!>\!S$, forms colourless needles, m. p. 190°, readily soluble in alkalis, even ammonium carbonate, and oxidised by ferric chloride to the *disulphide*, which crystallises in yellow prisms, m. p. 202°. *Dimethylaminothiodiazole*, $\begin{matrix}N{:}C(NHMe)\\ |\\ N{:}C(NHMe)\end{matrix}\!\!>\!S$, obtained as its hydrochloride, is precipitated from a concentrated aqueous solution of the latter by potassium carbonate. It forms coarse, colourless, leafy crystals, containing $1H_2O$, and melting at 175—176°. In contradistinction to the corresponding phenyl derivative it is not altered by boiling with mercuric oxide. It gives a stable nitrosoamine, m. p. 136°.

Hydrazinedicarbothioallylamide, m. p. 186°, was obtained in 80% yield by boiling alcoholic hydrazine hydrate for twenty minutes with allylthiocarbimide. The reaction with boiling hydrochloric acid, already described by Freund and Heilbrun (A., 1896, i, 415), furnished the basic *hydrazomethylthiazoline* (*dipropylene-ψ-hydrazodicarbothiamide*) and the acidic *allylaminothiodiazolethiol*. The basic substance agreed in its properties with the statements of Freund and Heilbrun (*loc. cit.*), except that on oxidation with mercuric oxide it gave an orange-red azo-compound, *azomethylthiazoline*,

$$\begin{matrix}CH_3\cdot CH\text{--}S\\ |\\ CH_2\cdot N\end{matrix}\!\!>\!C\cdot N{:}N\cdot C\!<\!\begin{matrix}S\text{--}CH\cdot CH_3\\ |\\ N\cdot CH_2\end{matrix},$$

m. p. 94°. This substance is more conveniently prepared by heating the alcoholic solution of the nitroso-compound of hydrazomethylthiazoline. Allylaminothiodiazolethiol, regarded by Freund as allyldithiourazole, must, however, have the constitution $\begin{matrix}N{=}{=}{=}{=}C(SH)\\ |\\ N{:}C(NH\cdot C_3H_5)\end{matrix}\!\!>\!S$, since it is strongly acidic, gives a disulphide (Freund's "azo-compound") on oxidation, a monomethyl derivative with methyl iodide, and a diacetyl derivative which readily loses one acetyl group.

A number of mixed hydrazinedicarboallylamides were prepared by combining allylthiosemicarbazide with various thiocarbimides, and their behaviour with hydrochloric acid was investigated. *δ-Allyl-α-carbothiomethylamide-thiosemicarbazide*, $C_3H_5\cdot NH\cdot CS\cdot NH\cdot NH\cdot CS\cdot NHMe$, m. p. 194°, and *δ-allyl-α-thiocarbanilidothiosemicarbazide*,

$$C_3H_5\cdot NH\cdot CS\cdot NH\cdot NH\cdot CS\cdot NHPh,$$

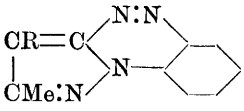
m. p. 183°, gave only the above-described allylaminothiodiazolethiol and methylamine, or aniline hydrochloride. On the other hand, the three following hydrazine dicarbamides underwent the alternative change exclusively, furnishing thiazoline derivatives and no products of an acidic character at all: *δ-allyl-α-thiocarbamidothiosemicarbazide*, $C_3H_5\cdot NH\cdot CS\cdot NH\cdot NH\cdot CS\cdot NH_2$, m. p. 184—185°, giving *1-methylthiazolylthiosemicarbazide*, m. p. 156°, *1-carbothioallylamidosemicarbazide*, $C_3H_5\cdot NH\cdot CS\cdot NH\cdot NH\cdot CO\cdot NH_2$, m. p. 189°, giving *1-methylthiazolylsemicarbazide*, $\begin{matrix}CHMe\cdot S\\ |\\ CH_2\text{---}N\end{matrix}\!\!>\!C\cdot NH\cdot NH\cdot CO\cdot NH_2$, m. p. 163°, and *δ-allyl-α-carbanilidothiosemicarbazide*, $C_3H_5\cdot NH\cdot CS\cdot NH\cdot NH\cdot CO\cdot NHPh$, m. p. 192°, giving only a minute quantity, however, of *1-methylthiazolyl-4-phenylsemicarbazide*, $\begin{matrix}CHMe\cdot S\\ |\\ CH_2\text{---}N\end{matrix}\!\!>\!C\cdot NH\cdot NH\cdot CO\cdot NHPh$, m. p. 157°.

In conclusion, the behaviour of propylene-ψ-thiocarbamide towards nitrous acid was investigated to see whether it behaved as a methylimino- or methylamino-thiazole. Since a stable nitrite and indications of a nitrosoamine were obtained, the former assumption is regarded as the more probable. G. F. M.

Diazo- and Azo-compounds of the Pyrazole Series. Ernst Mohr [with L. Kraft, E. Marx, F. Meyer, W. Schenke, L. Schmidt, and G. Warnecke] (*J. pr. Chem.*, 1914, [ii], **90**, 509—546).—The author has investigated the action of nitrous acid on 5-amino-1-phenyl-3-methyl-4-alkylpyrazoles, in which the 4-alkyl is methyl, ethyl, propyl or benzyl. When diazotised in excess of cold 0·33—2·33*N*-hydrochloric acid by means of sodium nitrite solution, these amines give the diazonium chlorides, which yield typical azo-β-naphthol colouring matters. It is remarkable that, under similar conditions, 5-amino-3-methyl-1-phenylpyrazole is diazotised only to the extent of 12%, the remainder being converted into 5-imino-4-oximino-1-phenyl-3-methylpyrazolone (compare A., 1909, i, 190); the influence of the 4-alkyl or hydrogen is thus clearly shown. In the diazotisation of the above aminopyrazoles, the solution assumes a lemon-yellow or yellowish-red colour and a flocculent, yellow precipitate separates at a later stage. These yellow substances are most probably analogues of those formed on diazotisation of the aminothiazoles (compare Hantzsch, A., 1890, 1165; Wohmann, A., 1891, 225; Schatzmann, A., 1891, 744, and Näf, A., 1891, 1515) and aminoindazoles (compare Bamberger, A., 1899, i, 543), and must be regarded as diazole hydrates or nitrosoamines.

When an acid diazo-solution of 5-amino-1-phenyl-3:4-dimethylpyrazole is added to excess of sodium hydroxide solution, the diazopyrazole undergoes conversion into the *iso*diazoxide and loses its capacity for coupling, this being restored on acidification. With the corresponding 4-benzyl derivative, a similar phenomenon is observed, but is complicated by the appearance in the alkaline solution of a bulky precipitate, the nature of which remains unexplained.

When the acid diazopyrazole solutions are introduced into boiling,



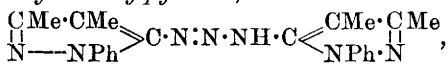
dilute sulphuric acid in order to obtain 5-hydroxypyrazoles, little or no nitrogen is liberated and separation of methylalkylpyrazobenzotriazines (annexed formula), in good yield and in a highly pure condition, takes place. Benzylmethylpyrazobenzotriazine, thus obtained, exhibits properties quite different from those of 1 : 4-diphenyl-3-methyldipyrazole obtained by Michaelis and Bender (A., 1903, i, 288). The preparation in this manner of 3 : 4-dimethylpyrazobenzotriazine gives also a small proportion of a product agreeing closely in composition with 1-phenyl-3 : 4-dimethylpyrazole, the formation of which, in absence of a reducing agent, would necessarily be accompanied by the oxidation of some other substance.

The apparently strange ring-closure occurring in the formation of the pyrazobenzotriazines is, indeed, markedly similar to the indazole and cinnoline ring-closures, according to which the diazo-group may undergo coupling with a neighbouring methyl, vinyl or phenyl group, but only under certain conditions, since it has not been found possible to convert *o*-diazodiphenyl into phenazone.

Bouveault (A., 1891, 51) states that 5-amino-1-phenyl-4-methyl-3-ethylpyrazole, prepared from propionitrile, gives on diazotisation a diazonium salt which, when boiled with alcohol, yields 1-phenyl-4-methyl-3-ethylpyrazole (compare Claisen and Meyerowitz, A., 1890, 357), and, when boiled with acidified water, is converted into 5-hydroxy-1-phenyl-4-methyl-3-ethylpyrazole. The author doubts both the character of this so-called diazonium salt and the identity of the pyrazole obtained with that of Claisen and Meyerowitz, and suggests that the 5-hydroxypyrazole may really be a pyrazobenzotriazine.

1-*Phenyl*-3 : 4-*dimethylpyrazole*-5-*azo*-β-*naphthol*, $C_{21}H_{18}ON_4$, forms brick-red needles, m. p. 189°, which show a green reflexion under the microscope and dissolve in concentrated sulphuric, hydrochloric and acetic acids, giving respectively violet, deep red and yellowish-red solutions.

Diazoaminophenyldimethylpyrazole,



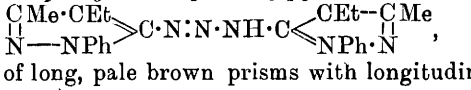
forms oblique, yellow plates, m. p. 127° (decomp.), and exhibits basic properties.

3 : 4-*Dimethylpyrazobenzotriazine*, $C_{11}H_{10}N_4$, forms lemon-yellow or brownish-yellow prisms or lozenge-shaped plates, m. p. 145°, b. p. 208—215°/15—17 mm., 225—226°/30 mm., 350—352° (decomp.)/753 mm. When the fused and subsequently solidified mass cools to 55—55·5°, distinctly audible crackling occurs and clouds of lemon-yellow dust are thrown several centimetres into the air; with thin layers, virtually the whole of the substance is expelled in this way. The phenomenon is probably due to the formation at about 55° or a higher temperature of a second modification. The compound has no odour and is quite stable in the air. It has very feeble basic properties and yields blood-red salts. Reducing agents attack it very slowly, and oxidising agents somewhat more readily.

1-*Phenyl*-3-*methyl*-4-*ethylpyrazole*-5-*azo*-β-*naphthol*, $C_{22}H_{20}ON_4$, forms arborescent masses of dark red prisms with green reflexion, m. p.

132°, and yields dark violet, deep red, and yellowish-red solutions in concentrated sulphuric, hydrochloric and acetic acids respectively.

5-*Diazoamino*-1-*phenyl*-3-*methyl*-4-*ethylpyrazole*,



forms bundles of long, pale brown prisms with longitudinal striations, m. p. 107° (decomp.).

3-*Methyl*-4-*ethylpyrazobenzotriazine*, $C_{12}H_{12}N_4$, forms lemon-yellow prisms or pale brown, rhombic plates, m. p. 106°, b. p. 210°/14 mm., and exhibits feebly basic properties.

1-*Phenyl*-3-*methyl*-4-*propylpyrazole*-5-*azo*-β-*naphthol*, $C_{23}H_{22}ON_4$, forms arborescent groupings of dark-red needles or prisms, m. p. 134°, and gives violet (like permanganate), intensely red and yellowish-red solutions in concentrated sulphuric, hydrochloric, and acetic acids respectively.

5-*Diazoamino*-1-*phenyl*-3-*methyl*-4-*propylpyrazole* (?), $C_{26}H_{31}N_7$, could not be obtained pure.

1-*Phenyl*-3-*methyl*-4-*benzylpyrazole*-5-*azo*-β-*naphthol*, $C_{27}H_{22}ON_4$, forms dark red needles or prisms showing green reflexion under the microscope, m. p. 162°, and gives violet, red and yellowish-red solutions in concentrated sulphuric, hydrochloric and acetic acids.

5-*Diazoamino*-1-*phenyl*-4-*benzyl*-3-*methylpyrazole*, $C_{34}H_{31}N_7$, forms bundles of transparent, pale brown prisms, m. p. 86°.

4-*Benzyl*-3-*methylpyrazobenzotriazine*, $C_{17}H_{14}N_4$, forms stable, yellow or yellowish-brown prisms or oblique plates, m. p. 128—130°, and gives blood-red solutions in mineral acids. Unlike 1 : 4-diphenyl-3-methyldipyrazole (compare Michaelis and Bender, *loc. cit.*), it does not yield an acetyl derivative when treated with boiling acetic anhydride. Its *silver* salt (?), $C_{17}H_{13}N_4Ag$, forms orange-yellow needles, m. p. 169—170°.

T. H. P.

Blue and Red Congo Dyes. The Theory of Indicators. A. Hantzsch (*Ber.*, 1915, **48**, 158—167).—The usual assumption that the Congo-red salts are azo-compounds, whilst the blue acid is a quinonoid substance, is not a complete explanation of the colour change when the dye is used as an indicator, for a red acid, optically identical with the alkali salts, may actually be isolated. The existence of this red acid accounts for the peculiar behaviour of Congo-red when used as an indicator in the presence of alcohol or acetone. For example, whereas an aqueous solution of Congo-red is rendered blue by carbon dioxide, an alcoholic solution is only gradually changed, through brown tones to blue, by relatively excessive addition of a mineral acid. Conversely, when alcohol or acetone is added to a solution just rendered blue by a mineral acid, the colour reverts to red. Under certain conditions the change from red to blue may be followed like a time reaction, such as keto-enol isomerisation. Congo-red is, therefore, in no sense of the word an indicator, except in pure aqueous solutions.

Within certain limits, all these solutions, red salt, red acid, and blue acid, can be obtained optically empty, as revealed by the ultramicroscope. Moreover, the change into the colloidal condition is not accompanied by a distinct change of colour, but only by gradual shading, due no doubt to the stronger reflexion of the macroscopic

particles. Indicator changes are not due to physical causes therefore, like alterations in the degree of dissociation or of dispersion, but are purely chemical in their origin, that is, due to isomerism.

As indicated above, isomeric Congo-acids have been isolated. They are in equilibrium in solution, and this equilibrium is dependent first of all on the nature of the solvent, and only secondly on the concentration of the hydrogen or hydroxyl ions. In aqueous solutions, one chromo-isomeride is "alkali-stable," the other "acid-stable," but in presence of alcohol the equilibrium is not so quickly displaced in favour of either form.

The absorption curves of the two acids are much the same in the ultra-violet, but absolutely different in the visible spectrum. The difference in constitution of the two isomerides must therefore be fundamental, and the red acid (I.), like the salts, is most probably azoid, whilst the blue acid (II.) is quinonoid.

I. $\left[O<\begin{matrix}O_2S-\\H_3N\end{matrix}>C_{10}H_5\cdot N{:}N\cdot C_6H_4\cdot\right]_2$ II. $\left[O<\begin{matrix}O_2S-\\H_2N\end{matrix}\gg C_{10}H_5{:}N\cdot NH\cdot C_6H_4\cdot\right]_2$

The blue Congo-acid was prepared in the crystalline state by Bogojavlenski (A., 1913, i, 301). It may be precipitated by ether from the red solutions in alcohol or acetone. The *red Congo-acid* is prepared by dissolving the blue acid in pyridine and heating the red, microcrystalline pyridine salt at 120—130°, when the base is expelled. There is no change in weight either in forming the red acid from the blue by this means or during the reversion to the blue acid which is effected by a trace of hydrochloric acid. Small quantities of the red acid may be obtained more conveniently by evaporating alcoholic or acetone solutions, the slight solubility of the dye being a limitation. The isolated red acid is, however, rather darker than the salts, which is doubtless due to the contamination with a trace of the blue acid.

Two isomeric acids may also be isolated from benzopurpurin.

J. C. W.

Isomerides of Helianthins and Aminoazobenzene Salts. A. Hantzsch (*Ber.*, 1915, **48**, 167—180. Compare A., 1913, i, 775). —The success which attended the isolation of red and blue Congo-acids (preceding abstract) has led the author to try again to prepare red and yellow helianthins in the solid state. The best results in this connexion have been obtained by evaporating alcoholic solutions of helianthin with about 10% of its sodium salt in platinum or silica vessels. The methyl-orange so depresses the hydrogen-ion concentration of the helianthin that the yellow form is prevented from changing into the red. The *brownish-yellow helianthin* (darker than the solutions because of contamination with a little of the red form) is considerably more soluble than the red modification and decomposes about 35° lower, namely, at about 200°.

Many other helianthins have been examined. With two exceptions, their red forms are stable and the yellow, either labile or unknown. The exceptions are the simplest helianthin, namely, anilineazobenzenesulphonic acid, and, strange to say, *dimethyl-o-toluidineazobenzenesulphonic acid.* In these cases, the stable form is yellow and the red form is labile. The red modifications are obtained by rubbing the yellow forms, but, whereas the red aniline derivative becomes yellow when merely breathed upon, the *o*-toluidine derivative has to be left in contact with water to bring this about.

A third class of chromo-isomeric helianthins consists of graphite-black products, which, like the corresponding aminoazobenzenes, contain free amino-hydrogen atoms. Such are the *monomethyl-*, *monoethyl-*, *monoamyl-* and *monobenzyl-helianthins*. They change into the red or yellow forms in the appropriate solvents. With a slight modification of the formula suggested for the black aminoazobenzene salts (*loc. cit.*) the two series are probably constituted thus :

$$ArNH\cdot N(HX){:}Ar{:}NR \text{ and } \begin{array}{l} Ar\cdot NH\cdot N{:}Ar{:}NR \\ | \qquad\quad \vdots \\ SO_3\text{——}H \end{array}$$

The isomerism of the various helianthins has been developed further by an examination of the absorption spectra. All yellow helianthin solutions are optically similar, in alcohol or alkalis, and the absorption curves are quite distinct from those of azo-compounds. Most of the red helianthin solutions show bands like those of magenta, that is, the red forms are quinonoid. The absorption curves are, moreover, very similar to those of the yellow helianthins. These red and yellow modifications must therefore be chemically similar, and are regarded as valency isomerides.

The abnormal red modifications are those derived from dimethyl-*o*-toluidine, namely, *dimethyl-o-toluidineazobenzene*, $C_{15}H_{17}N_3$, m. p. 98°, and the corresponding sulphonic acid. This is all the more remarkable since the dimethylaniline and the *o*-toluidine analogues are normal. The dimethyl-*o*-tolueneazobenzenesulphonic acid is useless as an indicator and the red solution shows an azoid absorption curve, like azobenzenetrimethylammonium salts, $PhN{:}N\cdot C_6H_4\cdot NMe_3X$. The hydrochloride of the dimethyl-*o*-toluidineazobenzene has the same azoid structure. It is the first genuine aminoazo-salt, and, therefore, is much more hydrolysed in solution than the red quinonoid aminoazo-salts. The abnormality of these dimethyl-*o*-toluidine derivatives must be due to a new case of steric hindrance. As usual, a salt is formed at the amino-group, but the three methyl groups then stand guard over the acid hydrogen atom and prevent the rearrangement into a quinonoid structure (I into II).

I. $NPh{:}N\cdot C_6H_3Me\cdot NMe_2HCl$ II. $NHPh\cdot N{:}C_6H_3Me{:}NMe_2Cl$.

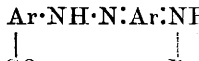
It is obvious, therefore, that conclusions drawn from mere outward appearance and not from a complete spectrographic examination may be very misleading.

The common methyl-orange itself exists in two chromoisomeric forms. The orange salt becomes deep red on rubbing, but this colour changes again to orange when the substance is breathed upon. They may also be valency isomerides.

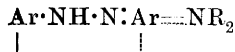
It is therefore established that there are four different solid isomerides of the helianthins, three of which exist in solution, namely, the azoid (I) and the black quinonoid (II) forms, and the orange-yellow (III) and red (IV) quinonoid, valency isomerides.

$$\begin{array}{l} Ar\cdot N{:}N\cdot Ar\cdot NR_2 \\ | \qquad\qquad \vdots \\ SO_3\text{————}H \end{array} \qquad (I.)$$

$$\begin{array}{l} Ar\cdot NH\cdot N{:}Ar{:}NR \\ | \qquad\quad \vdots \\ SO_3\text{——}H \end{array} \qquad (II.)$$



(III.)



(IV.)

J. C. W.

The Action of Alcoholic Solutions of Acids on Proteins. J. HERZIG and K. LANDSTEINER (*Biochem. Zeitsch.*, 1914, **67**, 334—337).—Serum proteins were treated with alcoholic hydrochloric and sulphuric acid solutions of various strength and at different temperatures, and the ethoxyl groups in the products obtained were estimated. There is very little more of NMe groups than exist in the untreated protein. Subsequent treatment of the alkylated proteins with diazomethane causes only a small addition to the ethoxyl (or methoxyl) groups, but a marked increase in the NMe groups. Reasons are given for supposing that the alkyl group is taken up without previous hydrolysis of the protein. S. B. S.

Well-characterised Organic Sulphur Compound obtained from Proteins by Treatment with Nitric Acid. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1914, **93**, 175—202).—When various proteins (serum-albumin, egg-albumin, casein, ovomucoid, hæmoglobin, keratin, glutin) are treated with nitric acid, a substance is formed which is identical with methanesulphonic acid, $CH_3 \cdot SO_2 \cdot OH$, and can be obtained and analysed in the form of its barium salt. The yield is from 1·4 to 12·4 grams of barium salt per kilogram of protein. The copper, lead, and potassium salts were also prepared and analysed. The author's further experiments indicate that the methanesulphonic acid does not arise from cystine, so that the existence of another sulphur-containing group in protein is probable.

Barium methanesulphonate crystallises with $1\frac{1}{2}H_2O$ at the ordinary temperature. The water is lost in a vacuum over sulphuric acid, and the salt crystallises anhydrous from warm solutions (compare Collmann, *Ann. Chem. pharm.*, 1868, **148**, 101). R. V. S.

Organic Phosphoric Acid Derivatives of Biochemical Importance. B. SJOLLEMA (*Chem. Weekblad*, 1915, **12**, 282—302).—The conclusion of the author's review (this vol., i, 182) of the present state of knowledge of the physiologically important organic derivatives of phosphoric acid. A. J. W.

Rotatory Power, Adsorption, and Centrifugation of Solutions of Pepsin. M. RAKUZIN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 141—143).—The success attending the examination of petroleum containing solid paraffin (*ibid.*, 1914, **46**, 592—593) has led the author to extend the application of the methods employed to other substances.

In aqueous solution, the $[\alpha]_D$ of pepsin ($c = 2{\cdot}0152$ p $5{\cdot}274$) is $+64{\cdot}5°$. Pepsin is adsorbed positively by alumina, 10% of the latter diminishing the rotation of a solution from $+3{\cdot}4°$ to $+3{\cdot}0°$ in one hour and negatively by gelatin, 3% of which increases the value

of D^{20} of a 5·248% solution of pepsin from 1·0198 to 1·0292 when boiled with it for a few minutes. After water has been boiled with 3% of gelatin, the solution obtained has D^{20} 1·0049 and α_D −3·8° in a 100 mm. tube. When submitted to centrifugation for one hour at 3000 revolutions per minute, pepsin solution develops only a very slight haze. T. H. P.

The Specificness and Multivalency of Trypsin, studied with Precipitation and Complement Deviation Methods. Francesco Marras (*Centr. Bakt. Par.*, 1914, i, **75**, 193—197).—Serum obtained by the injection of trypsin solutions possessing the capacity of acting on various proteins, exhibits similar behaviour in inducing precipitation and complement deviation phenomena with active and inactive trypsin, as does serum obtained by the action of trypsin solution which has been enfeebled by exposure to a temperature of 50°. The reaction is specific and cannot be induced by normal serum. The conclusion is drawn that trypsin is actually a single enzyme and not an enzyme-complex, since, if the latter had been the case, the precipitins and anti-substances arising from the action of so-called "glutinase" (trypsin heated at 50°) would have re-acted only with trypsin treated similarly and not with active trypsin—the hypothetical fibrinase, casease, albumase, etc. H. B. H.

Enzymic Decomposition of Hydrogen Peroxide. V. P. Waentig and O. Seche (*Zeitsch. physiol. Chem.*, 1914, **93**, 228—234 Compare A., 1913, i, 304).—Not only trypsin but also erepsin destroys the activity of catalase. The authors' experiments show that probably it is the peptolytic component of erepsin which is responsible for this reaction. The results confirm the view that catalase is of the nature of a protein. R. V. S.

The Influence of Acids on Dialysed Maltase. W. Kopaczewski (*Biochem. Zeitsch.*, 1914, **67**, 299—305).—The conditions of optimal concentrations of various acids on maltase action were tested with a dialysed preparation, and it was found that the action does not depend on the dissociation grade entirely, and the hydrion concentration in which optimal action was obtained was not the same for all acids. Other factors must, therefore, exert some influence on the action of acids. S. B. S.

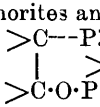
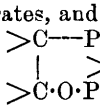
Preparation of a Diastatically Active Substance from Lactose. Theodor Panzer (*Zeitsch. physiol. Chem.*, 1915, **93**, 316—336).—When hydrogen chloride is allowed to act on lactose under the same conditions as were used in the case of diastase (A., 1913, i, 1007, 1119), no diastatically active substance is produced if the hydrogen chloride is removed by the vacuum process there described, but if the action of hydrogen chloride is followed by treatment with dry ammonia the preparation shows diastatic properties. Such diastatic preparations lose their diastatic power when their solutions are boiled. R. V. S.

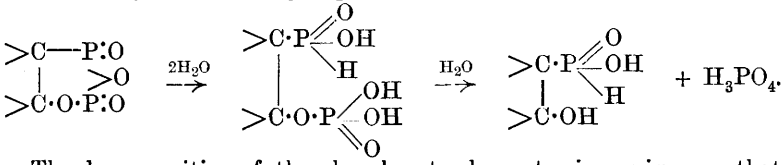
Diastase Preparations from Various Carbohydrates. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1915, **93**, 339—354. Compare preceding abstract).—The treatment with hydrogen chloride followed by evacuation or by treatment with dry ammonia has been applied to a number of carbohydrates with a view to the production from them of diastatically active substances such as can be produced from lactose. A weakly diastatic preparation can be obtained by the action of hydrogen chloride and ammonia on starch. Soluble starch, dextrin and gum arabic yielded active preparations in some experiments. Sucrose gave diastatic product only when treated with ammonia, hydrogen ch ide and then ammonia again. Maltose gave diastatic substances by both methods mentioned. Dextrose did not yield diastatic products except when treated in the same way as sucrose. Lævulose does not yield an active product by any method. Galactose gave a diastase with hydrogen chloride and ammonia in some experiments. None of these sugars gives more active preparations than lactose. R. V. S.

Behaviour of Various Substances towards Nitrous Oxide. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1915, **93**, 378—395).—The paper records the results of treating a considerable number of substances of very different types with nitrous oxide in the manner described for invertase and diastase (A., 1913, i, 780). None of the products obtained showed the behaviour of that obtained from diastase. R. V. S.

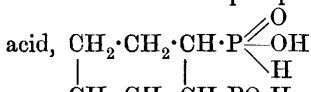
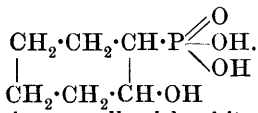
Oxidation Catalysis. II. The Behaviour of Unsaturated Compounds towards Phosphorus and Oxygen. RICHARD WILLSTÄTTER and EUGEN SONNENFELD (*Ber.*, 1914, **47**, 2801—2814).—In the earlier communication (A., 1913, i, 1200) it has been shown that osmium and, to a less degree, tellurium facilitate the oxidation of unsaturated compounds by gaseous oxygen, and colloidal osmium has now been found to be much more effective than the ordinary powder, an acetone solution containing 0·002 gram of the former being sufficient to replace 0·5 gram of the latter. Sulphur is found to be inactive in this direction, and the behaviour of phosphorus is essentially different from that of osmium, in that the phosphorus enters into the composition of the product. In the experiments with phosphorus, this element was used in a finely divided condition, obtained by shaking with warm water and then cooling; as benzene and the paraffins are unaffected by phosphorus and oxygen, benzene, light petroleum or *cyclo*hexane were used as solvents. The formation of the new phosphorus compounds can be easily observed by introducing the phosphorus together with a solution of the olefine into a test-tube and allowing access of air through a calcium chloride tube, when colourless needles appear in a few hours. For preparation on a larger scale a special apparatus is described.

Analysis of the products is not very trustworthy on account of their hygroscopic nature, but the results, together with those of measurements of the ratio, oxygen absorbed : olefine consumed : phosphorus consumed, prove the addition of the grouping P_2O_4 at the

double bond. Investigation of the velocity of absorption of the oxygen indicates a discontinuity in the curve after the absorption of a triatomic proportion of this element, and by checking the absorption at this point intermediate products containing the added group P_2O_3 can be obtained. These two classes of compounds, from their analogy in composition to the nitrosites and nitrosates of the terpenes, are termed phosphorites and phosphorates, and their behaviour suggests the structures  and  respectively. The phosphorates are very hygroscopic, colourless or pale yellow solids, vigorously decomposed by water, giving an ester acid which further undergoes hydrolysis into phosphoric acid and a phosphinic acid, thus:



The decomposition of the phosphorates by water is so vigorous that flame may ensue due to the formation of phosphine from the phosphinic acid, and to this source is also due the phosphine odour observable with the phosphorates and still more with the phosphorites.

cyclo*Hexene phosphorate*, $C_6H_{10}P_2O_4$, is a hygroscopic, pale yellow, crystalline powder with an odour of phosphine due to the action of moisture; when heated it decomposes generally near 160°. Water converts the phosphorate into *cyclo*hexanylphosphate-phosphinic acid,  , a gelatinous substance, the alkaline earth salts of which are more soluble in cold water than in hot. Nitric acid (40% concentration) oxidises the phosphorate and then causes hydrolysis to a cyclo*hexenephosphinic acid* (isolated as the sparingly soluble, amorphous *lead* salt), the formation of which is presumably due to elimination of the elements of water from the intermediately produced *cyclo*hexanolphosphinic acid,  .

Menthene phosphorate, $C_{10}H_{18}P_2O_4$, is a yellowish-white powder undergoing hydrolysis by water and nitric acid in the same way as the preceding substance. *Pinene phosphorate*, $C_{10}H_{16}P_2O_4$, and *trimethylethylene phosphorate* are similar.

Allyl alcohol behaved exceptionally, yielding a colourless, crystalline *substance* of the composition $(C_3H_6O)_3P_4O_6$.

Unsaturated acids and esters also yield phosphorates; thus, oleic acid gave an amorphous *phosphorate*, $C_{11}H_{12}O_2,P_2O_4$, olive oil gave an amber-like resin, whilst poppy oil produced a gelatinous compound.

A similar reaction has been observed qualitatively with many other ethylenic compounds.

The inhibitive effect of ethylenic compounds on the luminous oxidation of phosphorus, attributed by Schönbein to their effect on the ozone which acts as a positive catalyst, is explained by the authors as due to the formation of a thin film of resinous substances arising from the action of moisture on the primarily formed phosphorate.

Attention is drawn to the formation of phosphorates in the so-called "phosphorated oils," such as a solution of phosphorus in olive oil, and their possible influence on the medicinal properties. D. F. T.

New Method for the Preparation of Secondary Phosphinic Acids. A. Michaelis and Friedrich Wegner (*Ber.*, 1915, **48**, 316—318).—Triphenylphosphine oxide, Ph_3PO, m. p. 153°, is obtained when phenyl-*O*-oxychlorophosphine is added to an ethereal solution of magnesium phenyl bromide; when the reagents are mixed in the inverse order, small quantities of diphenylphosphinic acid are also obtained. The latter substance is, however, prepared in good yield by the action of piperidine-*N*-oxychlorophosphine, $C_5NH_{10}\cdot POCl_2$, on magnesium phenyl bromide in ethereal solution and has m. p. 190—191°. The primary product of the action is probably the *piperidide* of *diphenylphosphinic acid*,

$(C_5NH_{10}\cdot POCl_2 + 2MgPhBr = MgCl_2 + MgBr_2 + PPh_2O\cdot C_5NH_{10})$,

which is decomposed by hydrochloric acid, and this hypothesis receives confirmation from the synthesis of the piperidide from diphenyloxychlorophosphine and piperidine in ethereal solution and hydrolysis by acid with formation of diphenylphosphinic acid.

The reaction appears to be generally applicable; di-*p*-tolylphosphinic acid, m. p. 130—132°, dibenzylphosphinic acid, m. p. 180°, *di-o-tolylphosphinic acid*, and *dinaphthylphosphinic acid* have been prepared.

H. W.

Organic Compounds of Phosphorus with Nitrogen. II. A. Michaelis (*Annalen*, 1915, **407**, 290—332. Compare A., 1903, i, 379).—Tertiary *N*-phosphine oxides of the aromatic and of the aliphatic series, and also the anilides of aromatic phosphinic acids, are decomposed by heat, yielding a primary amine and an oxyphosphazo-compound (which is analogous to a diazoamine, containing :PO· in place of :N·). In a similar manner, tertiary *N*-phosphine sulphides yield thiophosphazo-compounds.

Oxyphosphazo-compounds are, in general, very stable, crystalline substances. Derivatives of the aliphatic series have the simple formula, whilst those of the aromatic series are dimeric. They are decomposed completely by vigorous reagents such as acids or alkalis, whereas mild reagents convert them into derivatives of iminophosphinic acid.

[With Julius Hochhut.]—The following esters are prepared by treating an alcoholic solution of the sodium alkyloxide with an ethereal solution of the alkylamine-*N*-phosphinyl chloride: *ethyl ethylamine*-N-*phosphinate*, $NHEt\cdot PO(OEt)_2$, faintly yellow liquid, b. p. 135°/25 mm.; *ethyl propylamine*-N-*phosphinate*, $C_7H_{18}O_3NP$, b. p. 112°/8 mm.; *ethyl* iso*butylamine*-N-*phosphinate*, b. p. 146°/14 mm.;

ethyl amylamine-N-*phosphinate*, b. p. 185°/25 mm. The phenyl esters are prepared from the alkylamine-*N*-phosphinyl chlorides and phenol dissolved in 10% sodium hydroxide: *phenyl ethylamine*-N-*phosphinate*, b. p. 205°/11 mm.; *phenyl propylamine*-N-*phosphinate*, b. p. 208°/8 mm.; *phenyl* iso*butylamine*-N-*phosphinate*, colourless needles, m. p. 58°, b. p. 218°/11 mm.

Bisethylamine-N-*oxychlorophosphine*, $POCl(NHEt)_2$, colourless needles, m. p. 74°, prepared from ethylamine-*N*-phosphinyl chloride and ethylamine in anhydrous ether, does not react with sodium ethoxide, but the corresponding bispropylamine and bisisobutylamine compounds yield *ethyl bispropylamine*-N-*phosphinate*, $OEt\cdot PO(NHPr^{\alpha})_2$, colourless needles, m. p. 108°, and *ethyl bis*iso*butylamine*-N-*phosphinate*, m. p. 123°.

[With Edgar Mentzel and Julius Hochhut.]—The following substances are obtained by heating the alkylamine-*N*-phosphine oxides or sulphides until the theoretical amount of the primary amine has been removed by distillation: *propyloxyphosphazopropylamine*,

$$NPr^{\alpha}{:}PO\cdot NHPr^{\alpha},$$

colourless needles, m. p. 213°; iso*butyloxyphosphazo*iso*butylamine*, $C_8H_{19}ON_2P$, m. p. 271° (these two compounds are converted into the preceding ethyl bisalkylamine-*N*-phosphinates by sodium ethoxide); *ethylthiophosphazoethylamine*, $NEt{:}PS\cdot NHEt$, prisms, m. p. 169°; *propylthiophosphazopropylamine*, $C_6H_{15}N_2PS$, m. p. 152°; iso*butylthiophosphazo*iso*butylamine*, m. p. 150°; and iso*amylthiophosphazo*iso*amylamine*, needles, m. p. 90°.

[With S. Nathanson, Emil Kahnemann, S. Danziger, and J. Hochhut.]—*Oxyphosphazobenzene chloride*, $NPh\langle^{POCl}_{POCl}\rangle NPh$, colourless needles or prisms, m. p. 228°, is obtained by heating aniline hydrochloride with a slight excess of phosphoryl chloride under quite definite conditions, namely, during fifteen hours at each of the temperatures 120°, 150° (during twenty-four hours), 170°, and 200°; other products of the reaction are aniline-*N*-phosphinyl chloride and oxyphosphazobenzeneanilide.

By the addition of oxyphosphazobenzene chloride to sodium phenoxide (2 mol.) suspended in dry benzene, phenyl aniline-*N*-phosphinate, m. p. 129° (*loc. cit.*), is obtained, but when the two substances are mixed in the reverse order, a *compound*, $C_{30}H_{26}O_5N_2P_2$, needles, m. p. 185°, is produced, which is a derivative of iminophosphinic acid.

By reaction with the hydrochlorides of primary or secondary amines in xylene at 150—180°, the chlorine atoms of oxyphosphazobenzene chloride are replaced by anilino-groups, and anilides, piperidides, etc., are produced: *oxyphosphazobenzenepiperidide*,

$$C_5NH_{10}\cdot PO\langle^{NPh}_{NPh}\rangle PO\cdot C_5NH_{10},$$

m. p. 223°, rhombic plates; *oxyphosphazobenzenemethylanilide*,

$$C_{26}H_{26}O_2N_4P_2,$$

colourless needles, m. p. 234°; *oxyphosphazo*-o-*toluenepiperidide*, rhombic octahedra, m. p. 195°, and the p-*isomeride*, m. p. 294°; *oxyphosphazo*-o-*toluenemethylanilide*, faintly yellow leaflets, m. p. 191°, and the p-*isomeride*, colourless leaflets, m. p. 251°. These substances are also

obtained by heating the arylamine hydrochloride and the arylamine-*N*-phosphinyl chloride.

When *p*-toluidine hydrochloride and phosphoryl chloride are heated as described above, the product is *oxyphosphazo*-p-*toluene*-p-*toluidide chloride*, $C_7H_7\cdot NH\cdot PO<^{N(C_7H_7)}_{N(C_7H_7)}>POCl$, colourless needles, m. p. 336°.

[With Bernhard von Gaza and Walter Rehse.]—By heating a homogeneous mixture of aniline hydrochloride, phenylphosphinyl chloride, and xylene at 120°, 150°, and 200° during one day at each temperature, *oxyphosphazobenzene*, $(C_{12}H_{10}ONP)_2$ or

$$NPh<^{POPh}_{POPh}>NPh,$$

colourless prisms, m. p. 290°, is obtained. It volatilises without decomposition above 360° under diminished pressure.

p-*Tolueneoxyphosphazobenzene*, $C_7H_7\cdot PO<^{NPh}_{NPh}>PO\cdot C_7H_7$, small plates, m. p. 273°, is obtained in a similar manner by heating aniline hydrochloride and *p*-tolylphosphinyl chloride. *Benzeneoxyphosphazo*-p-*toluene*, colourless, crystalline powder, m. p. 380°, the o-*isomeride*, m. p. 291°, *oxyphosphazo*-p-*toluene*, m. p. 312°, and the o-*isomeride*, m. p. 262°, and *benzeneoxyphosphazo*-*ψ*-*cumene*, m. p. 280°, have also been prepared.

By heating with arylamines at 130—150°, the preceding oxyphosphazo-compounds are converted into dianilides of the arylphosphinic acids. *Phenylphosphinanilide*-p-*toluidide*,

$$NHPh\cdot POPh\cdot NH\cdot C_7H_7,$$

needles, m. p. 200°, p-*tolylphosphindianilide*, m. p. 209°, p-*tolylphosphinanilide*-p-*toluidide*, m. p. 221°, p-*tolylphosphindi*-p-*toluidide*, m. p. 237°, and *phenylphosphinanilidepiperidide*, m. p. 212°, have been prepared.

Oxyphosphazobenzene is very sensitive to attack by water. When the compound is crystallised from moist benzene, a *derivative* of iminophosphinic acid, $OH\cdot POPh\cdot NPh\cdot POPh\cdot NHPh$, m. p. about 190°, and anilinophenylphosphinic acid are obtained. By heating with water at 150° and by heating with dilute sodium hydroxide, oxyphosphazobenzene is converted into the aniline hydrogen salt and the sodium salt of phenylphosphinic acid respectively. Corresponding, but more stable, derivatives of *p*-tolueneoxyphosphazobenzene have been prepared; the *substance*, $C_7H_7\cdot PO(OH)\cdot NPh\cdot PO(C_7H_7)\cdot NHPh$, m. p. 152°, *anilino*-p-*tolylphosphinic acid*, and *aniline hydrogen* p-*tolylphosphinate*, m. p. 203°, have been prepared By boiling with absolute alcohol, oxyphosphazotoluene yields *ethyl toluidinotolylphosphinate*,

$$C_7H_7\cdot NH\cdot PO(C_7H_7)\cdot OEt,$$

m. p. 53°. Similarly, *ethyl anilinophenylphosphinate*, m. p. 105°, and *methyl anilinotolylphosphinate*, m. p. 65°, have been obtained.

By heating with acetic anhydride, tolueneoxyphosphazobenzene yields an *acetyl* derivative of anilinotolylphosphinic acid,

$$NAcPh\cdot PO(C_7H_7)\cdot OH,$$

colourless leaflets, m. p. 162°. C. S.

A New Method for the Introduction of Arsenic into Organic Compounds. G. ROEDER and NICOLA BLASI (*Ber.*, 1914, **47**, 2748—2752).—The application of the mercury diaryls to the preparation of organic dichloroarsines has been found by Michaelis to be inconvenient and has been deserted in favour of the action of sodium on a mixture of an aryl bromide with arsenic trichloride. Contrary to the observation of Michaelis (A., 1902, i, 411, 515), the chloromercuri-compounds of the type R·HgCl, easily derivable from unsaturated substances in many cases, supply an easy method of producing such arsenic compounds by the reaction $R{\cdot}HgCl + AsCl_3 = HgCl_2 + AsRCl_2$. Such groups as the carboxyl, hydroxyl and amino-radicles which react with arsenic trichloride must be suitably protected in order to avoid the formation of hydrogen chloride, and the method is also limited by mercuration of a substituted benzene generally yielding only ortho- and para-compounds, of which the latter are alone capable of reacting readily with the arsenic trichloride. This characteristic difference between the substituent chloromercuri-groups in the ortho- and para-positions renders possible the production of a new class of compound containing both mercury and arsenic, the therapeutic value of which may be considerable.

The full experimental results are withheld for the present, but the following are given as examples. A mixture of 100 c.c. of pure benzene with 50 c.c. of an acetic acid solution of mercuric acetate was heated in a closed flask in boiling water for five hours. The benzene filtrate and washings were evaporated to a small bulk, and treated with an alcoholic solution of calcium chloride, when chloromercuribenzene separates. The insoluble residue from the first reaction contained poly-mercurated benzenes. When 30 grams of chloromercuribenzene were heated on the water-bath with 100 grams of arsenic trichloride for four to five hours, crystals of mercuric chloride separated and the supernatant liquid on distillation yielded phenyldichloroarsine, $C_6H_5AsCl_2$, b. p. 250—255°, a pungent liquid which could be converted by the action of chlorine and water into phenylarsinic acid, m. p. 158°. Bromomercuribenzene and iodomercuribenzene were also prepared in a similar manner, and were found to react satisfactorily, as also was the acetoxymercuri-compound, with arsenic trichloride. Chloromercuribenzene failed to react with antimony trichloride even in one hour at 200° (compare Michaelis, *loc. cit.*).

By interaction of chloromercurianisole with arsenic trichloride in the same proportions and under the same conditions as for the corresponding benzene compound, anisyldichloroarsine was obtained, and was further converted into anisylarsinic acid, m. p. 179—180°.

Chloromercuri-*o*-nitrobenzene and arsenic trichloride did not react even at 200°. D. F. T.

Secondary Aliphatic-Aromatic Arsinic Acids and their Reduction Products, especially 3 : 3′-Diamino-4 : 4′-dihydroxy-diphenyldimethyldiarsine. A. BERTHEIM (*Ber.*, 1915, **48**, 350—359).—With the object of preparing fatty-aromatic arsinic acids which would be of interest on account of their relationship to the

primary arsenic derivatives, on the one hand, and to cacodylic acid on the other, the author has continued the investigation of the action of alkyl haloids on aromatic arsenic oxides in the presence of alkali (compare Ehrlich and Bertheim, A., 1910, i, 451), and finds it to be of general application. Thus, phenylarsine oxide and methyl iodide yield *phenylmethylarsinic acid*,

$$AsPh(ONa)_2 + MeI = NaI + AsPhMeO{\cdot}ONa.$$

Iodides are more reactive than chlorides, but the hydriodic acid formed interferes with the isolation of the arsinic acid and must be removed either by precipitation with silver nitrate followed by precipitation of the silver salt of the arsinic acid or by treatment of the reaction mixture with freshly precipitated silver chloride. The secondary arsinic acids are well crystallised substances, which, like cacodylic acid, have an amphoteric character; they are extraordinarily resistant to oxidation by nitric acid.

3 : 3′-*Diamino*-4 : 4′-*dihydroxydiphenyldimethyldiarsine*,

$$As_2Me_2[C_6H_3(OH){\cdot}NH_2]_2,$$

is of interest on account of its near relationship to salvarsan. Unlike the latter, it is colourless and forms crystalline salts. Its toxicity is greater, and its therapeutic action less, than that of salvarsan.

Phenylmethylarsinic acid, AsPhMeO·OH, white, silky needles, m. p. 179·5° after previous softening, is prepared by the action of methyl iodide on a solution of phenylarsine oxide in alcohol and 10*N*-sodium hydroxide, and is purified through the *silver* salt, $C_7H_8O_2AsAg$. Its aqueous solution is acid to litmus, but not to methyl-orange. The *barium*, *lead* and *mercuric* salts are described. It yields a *hydrochloride* and a crystalline *nitrate*.

Phenylethylarsinic acid crystallises in colourless, four-sided prisms combined with pyramids, m. p. 108° (after previous softening) when rapidly heated. *Phenyl*isoa*mylarsinic acid*, prisms, has m. p. 108° after previous softening.

p-*Aminophenylmethylarsinic acid* is a crystalline powder, m. p. 201° after previous softening. The *silver* salt is described. The corresponding acetyl derivative is prepared from *p*-acetylaminophenylarsine oxide, and forms needles, m. p. 260° (decomp.) after previous softening.

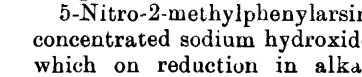
Phenylbenzylarsinic acid, shining needles, m. p. 206—207° after previous softening, is decomposed by hot concentrated hydrochloric acid into benzyl chloride and phenylarsine oxide or dichloride.

3-*Nitro*-4-*hydroxyphenylmethylarsinic acid* has m. p. 232—233° (decomp.). Attempts to reduce it directly to diaminodihydroxydiphenyldimethyldiarsine gave an impure product. Reduction can, however, be effected by first converting the nitro-compound into the *amino*-derivative, needles, m. p. 206—207° (decomp.) after previous darkening, by means of sodium hyposulphite followed by completion of the process by the use of hypophosphorous acid (D 1·136) and hydriodic acid (D 1·7). In this manner, the *hypophosphite* of 3 : 3′-*diamino*-4 : 4′-*dihydroxydiphenyldimethyldiarsine*,

$$C_{14}H_{18}O_2N_2As_2,2H_3PO_2,$$

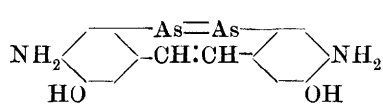
is obtained in white crystals. The corresponding *hydrochloride* is a white, crystalline powder. H. W.

Aromatic Arsenic Compounds. IX. Stilbenearsinic Acids and their Derivatives. P. KARRER (*Ber.*, 1915, **48**, 305—315).—The author has prepared a number of arsenostilbene derivatives which are of interest, since the phenyl radicles are joined by two bridges.

5-Nitro-2-methylphenylarsinic acid is transformed by moderately-concentrated sodium hydroxide into dyes of the type of Mikado brown, which on reduction in alkaline solution yield 5 : 5′-*diamino*-2 : 2′-*stilbenediarsinic acid*, from which 5 : 5′-*diamino*-1 : 1′-*arseno*-2 : 2′-*stilbene*,  , is obtained by means of hyposulphite.

Attempts to prepare a diaminodihydroxyarsenostilbene are also described. The nitro-4-hydroxy-*o*-tolylarsinic acid described by Bertheim is unsuited for this purpose, since it is not converted into a stilbene derivative by sodium hydroxide, and therefore does not contain the NO_2-group in the para-position to the methyl. This acid must therefore be 3-nitro-4-hydroxy-*o*-tolylarsinic acid. The failure of a stilbene synthesis cannot be attributed to the presence of the hydroxyl group, since a similar compound is readily obtained from 3 : 5-*dinitro*-4-*hydroxy*-o-*tolylarsinic acid*.

5 : 5′-*Diamino*-4 : 4′-*dihydroxy*-1 : 1′-*arseno*-2 : 2′-*stilbene* (annexed formula) is obtained by condensing 4-*chloro*-5-*nitro*-o-*tolylarsinic acid* to 4 : 4′-*dichloro*-5 : 5′-*dinitro*-2 : 2′-*stilbenediarsinic acid*. The chlorine of the latter is replaced by hydroxyl by the action of concentrated sodium hydroxide, and the resulting *compound* reduced to the required stilbene derivative. The physiological properties of the substances are disappointing.



o-Tolylarsinic acid, needles, m. p. 160° (compare Michaelis and La Coste, A., 1880, 396), is best prepared by the addition of sodium arsenite to a diazotised solution of *o*-toluidine, removal of excess of arsenic by hydrogen peroxide, and purification by means of the magnesium salt. It is converted by a mixture of concentrated sulphuric acid and nitric acid (D 1·49) into 5-nitro-*o*-tolylarsinic acid, needles, which darken at 230° and have m. p. 261°. The latter is converted by sodium hydroxide into a complex mixture of dinitroso-, azoxy- and azo-stilbenediarsinic acids, which is transformed by sodium hydroxide and zinc dust into *sodium* 5 : 5′-*diamino*-2 : 2′-*stilbenediarsinate*, $C_{14}H_{14}O_6N_2As_2Na_2,4H_2O$, from which the corresponding acid is readily obtained. Energetic reduction of the latter gives 5 : 5′-diamino-1 : 1′-arseno-2 : 2′- stilbene.

5 : 5′-*Dinitro*-2 : 2′-*stilbenediarsinic acid* is obtained by oxidation of the corresponding phenylarsinic acid by sodium hypochlorite and forms white crystals.

3 : 5-Dinitro-4-hydroxy-*o*-tolylarsinic acid, yellow needles, is prepared by nitration of 4-hydroxy-*o*-tolylarsinic acid; with concentrated sodium hydroxide solution it gives a stilbene dye.

4-*Chloro*-o-*tolylarsinic acid*, needles, m. p. 199° after softening at

195°, is formed by the addition of sodium arsenite to a diazotised solution of *p*-chloro-*o*-toluidine, and is nitrated by concentrated sulphuric and nitric acids at 30—40° to 4-chloro-5-nitro-*o*-tolylarsinic acid, leaflets, m. p. 215°. The latter yields a stilbene dye when treated with sodium hydroxide, in which, however, the chlorine atom is still present.

4 : 4′-Dichloro-5 : 5′-dinitro-2 : 2′-stilbenediarsinic acid, white, crystalline powder, is obtained by the action of sodium hypochlorite on an alkaline solution of 4-chloro-5-nitro-*o*-tolylarsinic acid, and is converted by further treatment with sodium hypochlorite and sodium hydroxide into 5 : 5′-dinitro-4 : 4′-dihydroxy-2 : 2′-stilbenediarsinic acid, from which, by reduction, 5 : 5′-diamino-4 : 4′-dihydroxy-1 : 1′-arseno-2 : 2′-stilbene is isolated. H. W.

Metallic Derivatives of *cyclo*Hexane. GERHARD GRÜTTNER (*Ber.*, 1914, **47**, 3257—3266. Compare A., 1914, i, 261, 891).—The differing behaviour of the mercury derivatives of *cyclo*hexane and benzene has led the author to investigate the *cyclo*hexyl derivatives of lead, tin and bismuth which are readily obtained by the action of magnesium *cyclo*hexyl haloids on the requisite metallic haloid. In general, these are as stable towards air as the corresponding phenyl derivatives: bismuth tri*cyclo*hexyl is, however, an exception, since it is readily and completely oxidised in ethereal solution.

*Lead tetra*cyclo*hexyl*, $(C_6H_{11})_4Pb$, forms canary-yellow leaflets or needles which become brown on exposure to light. It explodes feebly at about 225° when rapidly heated, and slowly decomposes above 200° with separation of lead. The *chloride*, $(C_6H_{11})_2PbCl_2$, pale yellow needles which become reddish-brown at 150° and deposit lead at 180°, is prepared by addition of the calculated quantity of a solution of chlorine in carbon tetrachloride to a solution of lead tetra*cyclo*hexyl in chloroform at 0° or by passing gaseous hydrogen chloride into lead tetra*cyclo*hexyl suspended in chloroform. The *bromide* forms pale yellow needles, which, when rapidly heated, become orange at 100°; on further rise of temperature, the colour fades, until, at 160°, the substance is almost white; at 225° lead separates suddenly. The *iodide* crystallises in orange-coloured needles and decomposes at 100°. The *sulphide*, $(C_6H_{11})_2PbS$, is prepared by passing a stream of hydrogen sulphide into a solution of the chloride or bromide in pyridine and precipitation with alcohol. It forms a pale yellow powder which blackens without melting at slightly above 100°. A nitrate could not be prepared, lead nitrate only being obtained by the action of dilute or concentrated nitric acid on lead tetra*cyclo*hexyl; the action of silver nitrate on the haloids gave silver haloid and a reddish-brown precipitate containing silver. The same reaction was shown by lead tetra*cyclo*hexyl and lead diphenyldi*cyclo*hexyl, but not by lead tetraphenyl. In the first two cases, silver derivatives of *cyclo*hexane appear to be formed, investigation of which is not yet complete.

*Lead diphenyldicyclo*hexyl*, $PbPh_2(C_6H_{11})_2$, pale yellow needles, m. p. 178—180°, to a clear yellow liquid which rapidly deposits lead, is prepared from magnesium *cyclo*hexyl bromide and lead diphenyl dibromide or from magnesium phenyl bromide and lead di*cyclo*hexyl

dibromide. It is much more readily soluble in alcohol, benzene, carbon tetrachloride or ethyl acetate than either lead tetraphenyl or lead tetra*cyclo*hexyl; the latter substances have closely similar solubilities. It reacts with bromine, iodine, hydrogen chloride and hydrogen bromide to yield lead di*cyclo*hexyl dihaloids, the two phenyl groups being replaced in every case.

It is remarkable that the lead *cyclo*hexyl derivatives are coloured, since, in general, organo-lead derivatives only show colour when they are unsaturated in character.

A halogen-free crystalline *substance*, probably bismuth tri*cyclo*hexyl, is obtained from bismuth bromide and magnesium *cyclo*hexyl bromide, the investigation of which is not complete.

[With MARTIN DITMAR.]—*Tin tetra*cyclo*hexyl*, $Sn(C_6H_{11})_4$, forms white, microscopic crystals, m. p. 248°. When warmed with stannic chloride in benzene solution, it gives a *product*, white needles, m. p. 264°, which is probably tin tri*cyclo*hexyl chloride; owing to the difficulty of completely removing stannous chloride, the analytical data are not quite exact. *Tin di*cyclo*hexyl dibromide*, obtained from tin tetra*cyclo*hexyl and bromine in carbon disulphide solution, forms long needles, m. p. 58°. The corresponding *di-iodide* crystallises in red needles, m. p. 145°, which readily lose iodine. H. W.

Mercury Compounds of the Pyrazolone Group. The Substitution Problem. WALTHER SCHRAUTH and HELLMUTH BAUERSCHMIDT (*Ber.*, 1914, **47**, 2736—2748).—Various pyrazolone derivatives have been submitted to the action of alcoholic mercuric acetate, with the result that all the compounds examined, namely, 1-phenyl-2:3-dimethyl-5-pyrazolone, 1-phenyl-3-methyl-2-ethyl-5-pyrazolone, 1-*p*-tolyl-2:3-dimethyl-5-pyrazolone, 1-*o*-tolyl-3-methyl-2-ethyl-5-pyrazolone, and 1-phenyl-3-methyl-5-pyrazolone, are found readily to take up four acetoxymercuri-groups together with a methoxyl group. If, however, the hydrogen atom in the 4-position adjacent to the carbonyl group is replaced by bromine, the methyl or the dimethylamino-group, no introduction of acetoxymercuri-groups occurs at the ordinary b. p. of the solution, and this is attributed to the hydrogen atom in this position playing the part of a "carrier" in the entry of the acetoxymercuri-groups in much the same way as the amino-hydrogen behaves in the mercuration of the alkyl anthranilates (Schoeller and Hueter, A., 1914, i, 892).

Mercuration of 1-phenyl-2:3-dimethyl-5-pyrazolone by warming at 60° with a methyl-alcoholic solution of mercuric acetate gave rise to 3 : 4-*diacetoxymercuri*-4-*methoxy*-1-*diacetoxymercuriphenyl*-2 : 3-*dimethyl*-5-*pyrazolone*, $C_6H_3(Hg{\cdot}OAc)_2{\cdot}N\langle^{CO-C(OMe){\cdot}Hg{\cdot}OAc}_{NMe{\cdot}CMe{\cdot}Hg{\cdot}OAc}$, rhombic leaflets of no definite m. p., but which sinter at 200—205°. Dilute hydrochloric acid at the ordinary temperature removes the mercury atom from the 4-position, this effect being probably due to the adjacent carbonyl group, giving 3-*chloromercuri*-4-*methoxy*-1-*dichloromercuriphenyl*-2 : 3-*dimethyl*-5-*pyrazolone*,

$$C_6H_3(HgCl)_2{\cdot}N\langle^{CO-CH{\cdot}OMe}_{NMe{\cdot}CMe{\cdot}HgCl}$$

a microcrystalline powder. The analogous 3 : 4-*diacetoxymercuri*-4-*ethoxy*-1-*diacetoxymercuriphenyl*-2 : 3-*dimethyl*-5-*pyrazolone*, obtained by mercuration in ethyl-alcoholic solution, formed colourless needles.

1-Phenyl-3-methyl-2-ethyl-5-pyrazolone on mercuration in solution in methyl alcohol formed 3 : 4-*diacetoxymercuri*-4-*methoxy*-1-*diacetoxymercuriphenyl*-3-*methyl*-2-*ethyl*-5-*pyrazolone*,

$$C_6H_3(Hg\cdot OAc)_2\cdot N\begin{cases}CO-C(OMe)\cdot Hg\cdot OAc\\ NEt\cdot CMe\cdot Hg\cdot OAc\end{cases},$$

prismatic needles, decomp. above 200° without melting. Treatment with hydrochloric acid converted this into 3-*chloromercuri*-4-*methoxy*-1-*dichloromercuriphenyl*-3-*methyl*-2-*ethyl*-5-*pyrazolone*,

$$C_6H_3(HgCl)_2\cdot N\begin{cases}CO-CH\cdot OMe\\ NEt\cdot CMe\cdot HgCl\end{cases}.$$

1-*p*-Tolyl-2 : 3-dimethyl-5-pyrazolone and 1-*o*-tolyl-3-methyl-2-ethyl-5-pyrazolone in methyl-alcoholic solution were converted into 3 : 4-*diacetoxymercuri*-4-*methoxy*-1-[*diacetoxymercuri*-p-*tolyl*]-2 : 3-*dimethyl*-5-*pyrazolone* and the corresponding 3 : 4-*diacetoxymercuri*-4-*methoxy*-1-[*diacetoxymercuri*-o-*tolyl*]-3-*methyl*-2-*ethylpyrazolone*, both of which under the action of hydrochloric acid lost the mercury atom from the 4-position, yielding *trichloromercuri*-derivatives.

Mercuration of 1-phenyl-3-methyl-5-pyrazolone at the ordinary temperature in methyl alcohol gave 3 : 4-*diacetoxymercuri*-4-*methoxy*-1-*acetoxymercuriphenyl*-3-*methyl*-5-*pyrazolone*,

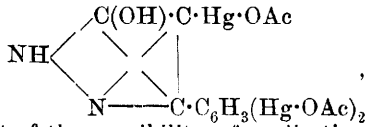
$$OAc\cdot Hg\cdot C_6H_4\cdot N\begin{cases}CO-C(OMe)\cdot Hg\cdot OAc\\ NH\cdot CMe\cdot Hg\cdot OAc\end{cases},$$

which crystallised with $1H_2O$, m. p. (anhydrous) 167° (decomp.); hydrochloric acid removes the 4-acetoxymercuri-radicle, leaving a *dichloromercuri*-compound. In boiling solution the product obtained is 3-*diacetoxymercuri*-4-*methoxy*-1-*diacetoxymercuriphenyl*-3-*methyl*-5-*pyrazolone*, $C_6H_3(Hg\cdot OAc)_2\cdot N\begin{cases}CO-C(OMe)\cdot Hg\cdot OAc\\ NH\cdot CMe\cdot Hg\cdot OAc\end{cases}$, crystalline, m. p. 225°.

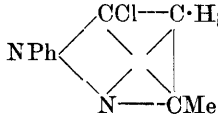
For the mercuration of 4-substituted pyrazolones of the preceding type, a temperature of 160° was necessary; under these conditions in the absence of solvent, 4-bromo-1-phenyl-2 : 3-dimethyl-5-pyrazolone yielded 4-*bromo*-4-*hydroxy*-3-*acetoxymercuri*-1-*triacetoxymercuriphenyl*-2 : 3-*dimethyl*-5-*pyrazolone*, $C_6H_2(Hg\cdot OAc)_3\cdot N\begin{cases}CO-CBr\cdot OH\\ NMe\cdot CMe\cdot Hg\cdot OAc\end{cases}$, decomp. at 225°.

In a similar manner, 1-phenyl-2 : 3 : 4-trimethyl-5-pyrazolone gave 4-*hydroxy*-3-*acetoxymercuri*-1-*triacetoxymercuriphenyl*-2 : 3 : 4-*trimethyl*-5-*pyrazolone*, $C_6H_2(Hg\cdot OAc)_3\cdot N\begin{cases}CO-CMe\cdot OH\\ NMe\cdot CMe\cdot Hg\cdot OAc,\end{cases}$ m. p. 237° (decomp.); on treatment with hydrochloric acid this produced 4-*hydroxy*-3-*chloromercuri*-1-*trichloromercuriphenyl*-2 : 3 : 4-*trimethyl*-5-*pyrazolone*, decomp. 245°.

3-Phenyl-5-pyrazolone reacted with a methyl-alcoholic solution of mercuric acetate, thus confirming the view as to the influence of the hydrogen in the 4-position; the product was 4-*acetoxymercuri*-3-

diacetoxymercuriphenyl-5 pyrazolone, 

, needles, decomp. near 250°; the effect of the possibility of enolisation is marked by the absence of any methoxy-group in the product; hydrochloric acid converted it into a *dichloromercuri*-compound, decomp. near 240°.

5-Chloro-1-phenyl-3-methylpyrazole in methyl-alcoholic solution was converted into *5-chloro-4-acetoxymercuri-1-phenyl-3-methylpyrazole*, 

, m. p. indistinct at 123°. With hydrochloric acid it yielded the corresponding *chloromercuri*-compound, needles, m. p. 165°. D. F. T.

Physiological Chemistry.

Rôle of Iron in the Respiration of the Egg of the Sea-Urchin. Some Oxidations which are Accelerated by Iron, Otto Warburg (*Zeitsch. physiol. Chem.*, 1914, **92**, 231—236).—The centrifugalised sediment of the eggs of *Strongylocentratus lividus* contains 0·02 to 0·03 mg. of iron to 100 mg. of nitrogen, which is equivalent to a few hundredths of a mg. of iron per 1 gram of the dried sediment. A suspension of the cell granules of the eggs, prepared by a method previously described (*Pfluger's Archiv*, 1914, **158**, 189), contains a corresponding quantity of iron. On the addition, to the freshly prepared suspension, of a trace of ferrous salt about equal in amount to that normally present in the suspension, the velocity of oxidation (respiration) is increased by 70—100%. Larger quantities of iron do not have a greater action, whilst smaller quantities have scarcely any effect. If the addition of the iron salt is delayed until the normal respiratory action of the granule suspension has subsided, the effect on the oxidative process is much smaller, which indicates that the substance which normally undergoes oxidation becomes used up during the respiratory process. Ethyl carbamate, which depresses the normal respiration of the granule liquid, also depresses, to the same extent, the enhanced respiration produced by the addition of the iron salt.

The addition to the suspension of cell granules of a substance, such as linolenic acid, which absorbs oxygen in the presence of ferrous salts, is followed by an increase in the amount of oxygen absorbed by the liquid. The suspension of granules behaves, therefore, as a catalyst, and the author draws the conclusion that probably the ferrous iron in the cell granules is responsible for the observed oxygen absorption. H. W. B

Physiological Diurnal Variations in the Amount of Sugar in the Blood of Man and the Effect of Ether and Chloroform Narcosis on it. ERNST HIRSCH (*Zeitsch. physiol. Chem.*, 1915, **93**, 355—369).—The amount of sugar in the blood of a healthy fasting man does not exceed 0·12%. In health the amount of blood-sugar varies considerably according to the quantity and nature of the food taken. The highest values are reached two and a half to four hours after the midday meal, and amount to 0·18%. In narcosis by chloroform, ether, or both, the blood-sugar rises; the upper limit is usually 0·19%; in one case 0·21% was found. In no case could sugar be detected in the urine. R. V. S.

The Second Dissociation Constant of Phosphoric Acid. L. MICHAELIS and T. GARMENDIA (*Biochem. Zeitsch.*, 1914, **67**, 431—438).—An electrometric method was employed. The second dissociation constant k_2 can be calculated from the formula

$$[H^{\cdot}]=k_2\,.\,[H_2PO_3]/[HPO_3].$$

Mixtures of KH_2PO_3 and Na_2HPO_3 were employed. Now

$$[H_2PO_3]=\delta_1[KH_2PO_3]$$

and $[HPO_3]=\delta_2[Na_2HPO_3]$. Hence $k_2=[H^{\cdot}]\delta_2/\delta_1$, where δ = dissociation grade. But in sufficient dilution $\delta_2=\delta_1$.

By measuring, therefore, the hydrion concentration of equimolecular proportions of the two phosphate salts in progressive dilutions, the value of k_2 can be found by extrapolation. From these experiments k_2 was found to be $0{\cdot}88\times10^{-7}$ at 25°. This value was also ascertained at 37°, and calculated also from the formula $d\log k/dT=U/4{\cdot}571T^2$, where U is the heat of reaction, $H_2PO_4\longrightarrow HPO_4'+H^{\cdot}$. This was found experimentally by determining the heat of reaction when Na_2HPO_4 reacts with an equimolecular proportion of hydrochloric acid. In order to obtain the ratio δ_2/δ_1 in animal fluids, the hydrion concentration of phosphate mixtures must be determined in the presence of varying amounts of sodium chloride. If $k_2'=k_2\,.\,\delta_2/\delta_1$, then [prim. phosphate]/[second. phosphate] $=[H^{\cdot}]\,.\,k_2'$. k_2' was determined directly in the presence of varying amounts of sodium chloride. After applying necessary corrections, it was found that the ratio of the primary to the secondary phosphates in the blood (with 0·9% sodium chloride) was about 1:5. This is the ratio in which they should exist in physiological saline solution, which should contain a total phosphate content between $N/50$ and $N/100$. S. B. S.

Oxidation of Cholesterol by the Blood. VIII. I. LIFSCHUTZ (*Zeitsch. physiol. Chem.*, 1914, **93**, 209—227).—If a mixture of dried blood (freed from "lipoids") and cholesterol is digested for some days at 60—65°, a considerable quantity (49·7%) of oxycholesterol is produced, as well as "cholesterol acids," giving a furfuraldehyde-sulphuric acid reaction similar to that obtained with the oxidation products of cholesterol prepared with benzoyl peroxide. As digestion proceeds, the amount of oxycholesterol decreases, and from further experiments it appears that this is due to a further

oxidation of the oxycholesterol. When the digestion takes place at 30—40° a maximum of 19·7% of oxycholesterol is produced.

Phytosterol in similar circumstances (60—65°) is less readily acted on; after fourteen days only 9·6% of oxyphytosterol is produced.

The paper records a number of observations regarding the colour reactions of the substances mentioned, and their application to analysis by spectrophotometrical means. R. V. S.

The Influence of Sodium Salicylate on the Uric Acid Concentration of the Blood. M. S. Fine and A. F. Chace (*Proc. Soc. expt. Biol. Med. New York*, 1915, **12**, 95).—Sodium salicylate, like atophan, increases the excretion of uric acid, and reduces the uric acid concentration of the blood to a-half or a-third. W. D. H.

Mechanical Injury to Red Corpuscles. Peyton Rous and J. R. Turner (*Proc. Soc. expt. Biol. Med. New York*, 1915, **12**, 100—108).—The fragility of red blood corpuscles varies greatly in different species, but they may be protected from hæmolysis during centrifugalising by adding a little gelatin to the Ringer's solution used for washing. Human blood cells are more resistant than those of other animals. W. D. H.

The Effect of Thyroparathyroidectomy on Blood Coagulation in the Dog. Sutherland Simpson and A. T. Rasmussen (*Proc. Soc. expt. Biol. Med. New York*, 1915, **12**, 96—98).—On the hypothesis that the parathyroids are concerned with calcium metabolism, these organs (with the thyroid) were removed. If the tetany produced is pronounced, the coagulation time of the blood is increased a little. This possibly indicates a low calcium content of the blood. W. D. H.

The Formation and Specificity of Blood Ferments as Revealed by the Application of Abderhalden's Dialysis Method. O. S. Parsamow (*Biochem. Zeitsch.*, 1914, **66**, 269—276).—Experiments were carried out on rabbits, the blood serum of which was found to be free of ferments. Various organs were then cut off from blood supply by ligature of the chief vessels through which the blood entered and left the organs, conditions of strict asepsis being observed in the operation. The proteolytic action of the serum was then tested on various organs of rabbits by means of Abderhalden's dialysis method. It was found that the serum contained, after this treatment of the animals, a ferment which was specific for the organ which had been excluded from the circulation, and not for others. The specificity was not, however, quite absolute, as the serum had a slight action on other organs. The observation of Petri and Heilner was confirmed, according to which the infection of an autogenous serum leads to the presence in the serum of a substance giving a positive ninhydrin reaction with muscular tissue. This does not happen, according to the author, when plasma instead of serum is injected. It was found

also that the administration of trypsin *per os* leads to the presence in the blood of ferments producing a positive ninhydrin reaction with various organs, and attention is called to the fact that a positive reaction may be therefore due in certain cases to a hypersecretion of ferments in the alimentary tract. S. B. S.

The Ferment and Anti-ferment Action of the Serum. GEORG HÄLSEN (*Biochem. Zeitsch.*, 1914, **67**, 277—297).—Investigations were carried out on the action of various sera on placental and tumorous substances, both the optical and dialysis methods of Abderhalden being employed. In 21 out of 27 cases the results obtained by the optical method harmonised with the clinical diagnoses. The two methods harmonised in 20 out of 28 cases with one another, and these cases corresponded 19 times with the diagnosis. The content of the sera in peptolytic ferment tested with glycyltryptophan was not found to run parallel with the dialysis results, neither was there any parallelism between the antitryptic content of sera and a positive result with the Abderhalden reaction. More often, in the cases of carcinoma, there was an abnormally high antitryptic content than a positive Abderhalden reaction. In only a very few cases the glycyltryptophan test, the antitryptic test, and the two Abderhalden reactions all harmonised. S. B. S.

The Ninhydrin Reaction of Peptones. Addendum to Hälsen's Paper on "the Ferment and Anti-ferment Action of Serum." ERNST FRÄNKEL (*Biochem. Zeitsch.*, 1914, **67**, 298).—Attention is called to the fact that there is a great difference in the sensitiveness of the various peptones to the ninhydrin reagent; thus, carcinoma peptone gives a positive result in the dilution 1 : 250, and a negative result in the dilution 1 : 300, whereas silk peptone gives a positive result in the dilution 1 : 8000, and a negative in the dilution 1 : 9000. S. B. S.

Lipoids of Human Serum and the Estimation of Lipoids. W. KLEIN and L. DINKIN (*Zeitsch. physiol. Chem.*, 1914, **92**, 302—330).—The amount of cholesterol in normal human serum is about 177 mg. per 100 c.c. of serum. It is not increased in cases of carcinoma, but in other diseases, especially those in which a positive Wassermann reaction is observed, the cholesterol content of the serum may rise to above 300 mg. per 100 c.c.

For the estimation of cholesterol in serum, Autenrieth and Funk's method is recommended. The serum is hydrolysed, the cholesterol extracted with ether, and, after evaporation of the solvent, the cholesterol dissolved in chloroform and estimated colorimetrically by the relative intensity of colour produced on the addition of acetic anhydride and sulphuric acid. The remaining lipoids in the serum are estimated by first drying the serum with anhydrous sodium sulphate (Fränkel and Elfer, A., 1910, ii, 1081) and then extracting with a mixture of alcohol and ether (2 : 1). The extract is then divided into fractions soluble in ether, insoluble in ether, soluble in acetone, etc. Tables are given showing the

variations in the amounts of these fractions in cases of paralysis, tabes, and other diseases. H. W. B.

The Action of Invertase on the Utilisation of Sucrose and Dextrose in the Animal Organism. S. La Franca (*Biochem. Zeitsch.*, 1914, **67**, 232—242).—If considerable quantities of sucrose are injected into a dog, and also invertase, only a portion of the injected sugar will be excreted in the urine; it is inverted in the blood, and the monosaccharides produced are oxidised. The larger the amount of invertase injected, the smaller the amount of sugar which is excreted. The influence of the ferment on the organism lasts for some time after the injection. The invertase also promotes the utilisation of the monosaccharides, for if a large amount of dextrose is injected and then sufficient invertase, the glycosuria is almost abolished. The action of invertase on glycosuric animals is as follows: (*a*) It neither inhibits the onset of adrenalin glycosuria nor banishes it when it has once started; (*b*) it diminishes pancreatic diabetes, and even stops it when the dose is sufficiently large; (*c*) it has no influence on phloridzin glycosuria. S. B. S.

The Secretion of Gastric Juice in Man. A. J. Carlson (*Amer. J. Physiol.*, 1915, **37**, 50—73).—Observations extending over three years were made on a healthy man with a gastric fistula; the œsophagus was occluded so that the stomach contents contained no saliva; there was little or no regurgitation from the duodenum except in the morning, when bile was usually found. The gastric glands are never quiescent, and the juice secreted in an empty stomach digests itself. The fluid content of the "empty" stomach varies from 8 to 50 c.c., with an average of 20 c.c. Chewing of indifferent substances does not augment secretion, but the sight, smell, and thought of palatable food usually produce a slight transitory increase; the amount secreted on mastication of palatable food varies with its palatability; fifteen to twenty minutes after chewing ceases the usual level is reached. The continuous secretion is rich in pepsin, but poor in hydrochloric acid; the percentage of this acid in the gastric contents never rose above 0·2. It is calculated that the adult normal person secretes during an average dinner 700 c.c., and in the twenty-four hours 1500 c.c. of gastric juice. W. D. H.

Erepsin. S. Korzarenko (*Biochem. Zeitsch.*, 1914, **66**, 344—367).—Large amounts of erepsin are found in the mucous membrane of the intestine, and must play a considerable part in the digestive process. The ferment is destroyed at 58°, and by remaining for a long time at 50°. It is destroyed by both organic and inorganic acids, in concentrations of from 0·02 to 0·04% within one hour. Lower concentrations inhibit the action without destroying the ferment. The action of alkalis is also injurious, but not to the same extent as that of acids. Solutions of 0·06 to 0·13% destroy the ferment within one hour. Sodium salts diminish the action, whereas potassium salts are without influence. Sulphates and

phosphates are without action, but salts of other acids diminish the action. Alanine and glycine in concentrations of 3—4% are without action. Alcohol in concentrations above 2% inhibits the action. Human pancreatic juice contains a minute amount of erepsin; that of dog contains still less. Of other organs, the liver contains the largest amount of this ferment; after this the kidneys and the mucous membrane of the small intestine contain most; traces only are found in muscles, spleen, and serum. There is an increase of ereptic properties in all organs after phosphorus poisoning. The increased action of erepsin due to blood-serum is small, and is due partly to the ferment contained in this fluid. S. B. S.

Experiments with Diets with One Constituent. I. The Distribution of Water and Œdema Formation on Addition of Salts. PAUL TACHAU (*Biochem. Zeitsch.*, 1914, **67**, 338—348).—The body of the white mouse, exclusive of the intestines, contains about 74·5% of water. Nutrition with diets containing excess of sugar, with continuous addition of inorganic salts (sodium chloride, phosphate, and lactate), does not, as a rule, result in any change in this number, even when it leads to œdema. Insufficient amounts of a suitable diet give rise to only a small diminution of the water-content. The percentage of chlorine in the body is not increased by an increased administration of sodium chloride; neither does this substance lead to an increased osmotic pressure. The formation of an œdema cannot be ascribed to the retention of water, but appears to be due rather to a difference in its distribution resulting in the administration of salts. S. B. S.

The Action of Extracts of Organs on the Heart. E. BÜRGI and C. F. VON TRACZEWSKI (*Biochem. Zeitsch.*, 1914, **66**, 417—436).—The action of the extracts of the following organs on the heart of *Rana esculenta* was investigated by Engelmann's method: thyroid, pituitary body, a combination of these two extracts, adrenals, thymus, and testicles. The extract of each organ has a characteristic action, which is illustrated in the paper by numerous tracings, from which alone a clear conception of the actions can be obtained. A combination of all extracts in normal proportions appears to act as a general stimulant of heart action without fundamentally altering its character. S. B. S.

Protein Storage in the Liver After Enteral and Parenteral Administration of Various Degradation Products of Proteins. C. E. CAHN-BRONNER (*Biochem. Zeitsch.*, 1914, **66**, 289—307).—Experiments were carried out with *Salamandra maculata*, the protein storage of the liver being determined by Berg's histological method. It was found that various degradation products of proteins, including the part of Witte's peptone which is insoluble in alcohol, and both the alcohol-soluble and -insoluble portions of pancreatised meat, could produce protein-storage in the liver when administered *per os*. There are factors which inhibit this storage, amongst which may be mentioned the peptocyme action, which is

due to substances in Witte's peptone which are contained in the alcohol-soluble portion (Pick). The administration of the whole peptone, therefore, does not result in protein-storage in the liver. In no case did storage result after administration parenterally of the above substances S. B. S.

Formation of Acetoacetic Acid from Glycollic Acid in the Liver. ADAM LOEB (*Zeitsch. physiol. Chem.*, 1914, **93**, 270—275).—The author has made experiments to discover why Mochizuki (A., 1913, i, 1277) and Honjio (A., 1914, i, 779) found no formation of acetoacetic acid to follow perfusion of a liver with glycollates, whilst Embden and Loeb (A., 1913, i, 1411) did observe a production of acetoacetic acid in these circumstances. The author now finds that the difference is probably due to the larger quantities of glycollate used by Embden and Loeb (4 grams as compared with 2 grams). Other differences in the conditions employed may also have had an influence. The experiments make it unlikely that glycollates form an intermediate step in the production of acetoacetates from acetates in the liver. R. V. S.

Physiology of the Thyroid Gland. VI. The Storage and Attachment of Iodine in the Body. F. BLUM and R. GRÜTZNER (*Zeitsch. physiol. Chem.*, 1914, **92**, 360—382).—The following methods for estimating separately the free (inorganic) and the combined (organic) iodine in animal tissues have been investigated: (1) extraction of the inorganic iodide from the dried material by a solvent in a Soxhlet apparatus (2) removal of the inorganic iodide by dialysis; (3) liberation of free iodine from the iodide, and subsequent volatilisation in a current of air. The results obtained were unsatisfactory in every case.

Lymph and the lymphatic glands in the neighbourhood of the thyroid gland do not contain any iodine. Other organs of the body (liver, kidney, spleen, heart, and lungs) were found to be free from organic iodine, although occasionally traces of inorganic iodine were detected. Even after the administration of iodides (to dogs), the thyroid gland is the only organ containing organically combined iodine, traces of iodine found in the liver being in the form of unchanged iodide. The thyroid is therefore the only organ in the body capable of transforming iodides into iodine-protein compounds, and of thus acting as a storage for iodine in the body. H. W. B.

The Presence of a Substance which Inhibits Coagulation in the Female Sexual Organs and Placenta. TORAHIKO FUJII (*Biochem. Zeitsch.*, 1914, **66**, 368—388).—Substances can be readily extracted by salt solution from human ovaries, uterus, or tubes which have a strong inhibitory action on the coagulation of blood. The ovaries yield the most powerful inhibitory extracts. The mucous membrane of the uterus yields a stronger extract than the uterine muscles. From the sexual organs of animals inhibitory substances could also be extracted. In the dog, the ovaries gave a

more powerful extract than the uterus, whereas in the rabbit the reverse is the case. Human placenta, when free from blood, also yield inhibitory extracts, but the action is masked by coagulating substance when the blood is not removed before making the extract. These extracts also contain an ereptic ferment. The amount of inhibitory substance which can be extracted is increased if the placenta are first submitted to autolysis. S. B. S.

The Serum Nuclease of Pregnant Women and of Nephritic Patients. NINA KOTSCHNEV (*Biochem. Zeitsch.*, 1914, **67**, 163—165).—A polarimetric method for investigating the nuclease action was employed. In sixteen nephritic cases the serum-nuclease action showed no deviation from the normal, whereas the sera of twenty-five pregnant women showed a slightly increased nucleolytic action which increased towards the end of the pregnancy. S. B. S.

The Swelling of Muscle. K. VON KÖRÖSY (*Zeitsch. physiol. Chem.*, 1914, **93**, 154—174).—The change in weight of a gastrocnemius of the frog when kept for an hour in solutions of different concentrations of dextrose, sucrose, sodium chloride, potassium chloride, and calcium chloride proceeds almost identically in all cases. Avogadro's hypothesis therefore holds, not only for the region of isotonicity, but also for all other concentrations. An apparent exception is found in the fact that the absorption of water by the muscle is relatively stronger in dilute solutions than in more concentrated ones. This difference is more marked when the duration of the experiment is fifteen minutes than when it is one hour. When the duration of the experiment is short, the change in weight of the muscle depends on the rate of movement of the water under osmotic pressure. When the muscles have remained for seventeen hours in the solutions no sort of agreement with Avogadro's hypothesis exists. Plates of gelatin, however, behave similarly in many respects, and this indicates that a colloidal swelling is in question. Pieces of muscle behave according to Avogadro's hypothesis when the duration of the experiment is fifteen minutes, but their behaviour changes much more quickly than that of the intact muscle. R. V. S.

Formation of Lactic Acid and Phosphoric Acid in the Expressed Juice of Muscles. GUSTAV EMBDEN, WALTER GRIESBACH, and ERNST SCHMITZ (*Zeitsch. physiol. Chem.*, 1914, **93**, 1—45. Compare Embden, Kalberlah, and Engel, A., 1912, ii, 1071; Kondo, A., 1912, ii, 1072).—This paper deals with the "lactacidogen" postulated by the authors in the papers cited. A large number of experiments under various conditions is described in detail, and from them the authors deduce the result that lactic acid and phosphoric acid are formed in expressed muscle juice in equimolecular quantities, at any rate in certain experimental conditions. When hexose-phosphoric acid is added to the juice the production of lactic acid and phosphoric acid is increased, although not in equimolecular proportions. R. V. S.

Behaviour of Lactic Acid and Phosphoric Acid in the Expressed Juice of the Uterus. MARTHA COHN and RUDOLF MEYER (*Zeitsch. physiol. Chem.*, 1914, **93**, 46—53. Compare preceding abstract).—The work of Embden, Griesbach, and Schmitz, and of their predecessors, was carried out with striped muscle. The authors have repeated it, using the plain muscle of the uterus. The expressed juice on keeping a short time at 40° does not produce lactic and phosphoric acids, or only in very small amount. If instead of the juice a paste of the organ is used, no lactic acid is formed, but the production of phosphoric acid can be observed.

R. V. S.

Action of the Expressed Juice of the Uterus on Hexose-phosphoric Acid. HANS HAGEMANN (*Zeitsch. physiol. Chem.*, 1914, **93**, 54—59. Compare preceding abstracts).—When hexose-phosphoric acid is added to the juice, lactic acid and phosphoric acid are produced in about the same amount as when the juice of striped muscle is employed. R. V. S.

Formation of Lactic Acid and Phosphoric Acid in Frog's Muscle. I. FRITZ LAQUER (*Zeitsch. physiol. Chem.*, 1914, **93**, 60—83. Compare preceding abstracts).—The amount of phosphoric acid found in the muscle varied but little in most experiments, and was not altered when the muscle was exhaustively stimulated by electrical means. Heat rigor led (in five cases out of six) to a perceptible increase in the phosphoric acid found, the muscle being morphologically intact. When the muscle was previously finely divided, heat rigor led to a much greater production of phosphoric acid. The formation of the acid is rapid, being complete in one hour. Fletcher and Hopkins (*J. Physiology*, 1906, **35**, 247) have investigated the formation of lactic acid in frog's muscle. The author has obtained similar results, and also finds that the addition of sodium hydrogen carbonate to a paste of muscle increases the production of lactic acid on warming. This indicates that the maxima of lactic acid formation observed by Fletcher and Hopkins are due to the increasing concentration of the acid. R. V. S.

Formation of Lactic Acid and Phosphoric Acid in Carp's Muscle. MARTHA COHN (*Zeitsch. physiol. Chem.*, 1914, **93**, 84—93. Compare preceding abstracts).—The expressed juice of the skeletal muscles of the fresh-water carp produces on keeping at most only very small quantities of lactic and phosphoric acids. Hexose-phosphoric acid is decomposed into lactic and phosphoric acids by the juice at 40° in a short time. A paste of the muscle forms considerable quantities of lactic acid and phosphoric acid on keeping for a short time. R. V. S.

Chemistry of Lactacidogen. I. Attempts at Isolation. GUSTAV EMBDEN and FRITZ LAQUER (*Zeitsch. physiol. Chem.*, 1914, **93**, 94—123. Compare preceding abstracts).—Extracts (freed from

protein) of the expressed juice of muscles or of muscle paste yield with barium hydroxide a precipitate which contains phosphates and organically combined phosphorus. When this precipitate is decomposed with sulphuric acid, the solution obtained reduces Fehling's solution strongly, gives a pronounced orcinol reaction, and is strongly optically active. If this liquid is added to the expressed juice of muscle the production of lactic acid and phosphoric acid is increased, so that it contains lactacidogen. The lactacidogen can be precipitated from the solution partly by means of lead acetate, and the rest is precipitated by basic lead acetate and ammonia. If these precipitates are freed from lead, the resulting solutions increase the production of lactic acid and phosphoric acid when added to muscle juice. If the expressed juice of muscle is kept at 40° for two hours, the reducing substance precipitable by barium hydroxide almost completely disappears.

In some of the experiments in which lactacidogen solutions were added to muscle juice, lactic acid was formed without a corresponding amount of phosphoric acid.

The barium hydroxide precipitate contains other organic phosphorus compounds. One such can be precipitated with acetone from the lead acetate precipitate after removing the lead. It contains a pentose group, and adenine; it is without influence on the formation of lactic acid and phosphoric acid in muscle juice.

R. V. S.

Decomposition of Hexose-phosphoric Acid and Lactacidogen by the Expressed Juices of Some Organs. GUSTAV EMBDEN, WALTER GRIESBACH, and FRITZ LAQUER (*Zeitsch. physiol. Chem.*, 1914, **93**, 124—144. Compare preceding abstracts).—The organs used were the kidney, testis, and pancreas of the ox. The expressed juice of the kidney or of the testis produces small quantities of lactic acid on keeping, but little or no phosphoric acid. These juices produce lactic acid and phosphoric acid from hexose-phosphoric acid or from lactacidogen solutions. Expressed juice from the pancreas acts similarly, but much more feebly. R. V. S.

The Influence of the Mechanical Destruction of Cell Structure in the Different Oxidation Processes of the Animal Tissues. F. BATELLI and L. STERN (*Biochem. Zeitsch.*, 1914, **67**, 443—471).—The phenylenediamine oxydone of different tissues remains intact after complete destruction of the cells. The succinic oxydone in several tissues (muscles, heart, kidneys) also remains intact, whereas in other tissues (liver of different animals) it undergoes a weakening. The stable oxydones cannot be extracted from the intact tissues by water, but they can be extracted after destruction of the cells if the water is slightly alkaline. On adding acetic acid to the extract they are precipitated, and exert their activity when re-dissolved in weak alkali. In aqueous solution their behaviour towards various reagents is the same as when in the cells. They are destroyed or very much weakened when heated at 60°, and are rapidly destroyed by trypsin. They undergo irre-

versible destruction when treated with anæsthetics in relatively weak solutions. They are, in the opinion of the authors, proteins, and not related to the lipoids. The citric oxydone is rapidly destroyed when the cells are broken up. The primary respiration also appears to be markedly injured by the destruction of cells, although the intensity does not appear to depend on the number of intact cells. The active substances of the accessory respiration and oxydases are not present in larger quantities in the extracts made from tissues with disintegrated cells than in those made from tissue with cells intact. These substances appear, therefore, to pass the cell membrane. S. B. S.

Conjugated Glycuronic Acids. III. Hydrolysis of Orcinol- and Phloroglucinol-glycuronic Acids by Tissue Juices. Yoshita Sera (*Zeitsch. physiol. Chem.*, 1914, **92**, 261—275. Compare A., 1914, i, 290, 694).—From the results of polarimetric measurements the author concludes that orcinol- and phloroglucinol-glycuronic acids, and also urocholic acid, which are not resolved by emulsin, are hydrolysed by various extracts of animal tissues (liver, spleen, and kidney of ox; liver of rabbit; liver, spleen, and kidney of dog; and liver of hen). Since the boiled extracts are without action, the observed hydrolysis is probably of enzymic nature. Extracts of the blood of ox or dog do not possess any hydrolytic power over these conjugated glycuronic acids. H. W. B.

Action of Tissue Extracts on Uric Acid Investigated by Means of Folin's Method. Georg Landmann (*Zeitsch. physiol. Chem.*, 1914, **92**, 416—444).—Small quantities of uric acid have been added to various tissue extracts, and the amounts present after successive time intervals estimated by a modification of Folin's method (A., 1913, ii, 162). The mixtures were kept at various temperatures, toluene being added to prevent putrefaction.

Uric acid is gradually destroyed by extracts of the livers of cat, dog, and rabbit, the destruction being complete in from eight to thirty days. The disappearance is hastened by oxygenation and by raising the temperature to 45°. Bird's liver does not appear to possess the power of decomposing uric acid; on the contrary, the amount of uric acid in the tissue extract tends to increase. Extracts of ox spleen also have a distinct power of synthesising uric acid, especially if excess of purines (adenine, guanine, hypoxanthine, xanthine) are added. Synthesis of uric acid from adenine or guanine by liver extracts of dog or cat could not be obtained. These results confirm the view that the liver and spleen, in mammals, are antagonistic in their action on uric acid. H. W. B.

Compounds of the Type of Chondroitinsulphuric Acid. Federico Alzona (*Biochem. Zeitsch.*, 1914, **66**. 408—416).—The substances were extracted from the tissues by 2% potassium hydroxide. The proteins were separated by Levene's picric acid method, and the nucleins were precipitated by calcium chloride from alkaline

solutions. The crude products were purified by throwing the concentrated syrupy aqueous solutions into glacial acetic acid. Chondroitin-like substances were obtained from cartilage of the nasal septum of pigs, from the mucous membrane of the small intestine of ox, from mucous membrane of pig's stomach, from human prostate glands, and from ox-thyroids. Although these substances were not, apparently, identical, they all had the general characters of chondroitinsulphuric acid. S. B. S.

The Physical Chemistry of Intra vitam Staining. RUDOLF HÖBER (*Biochem. Zeitsch.*, 1914, **67**, 420—430).—It was found, in the investigation with a large number of drugs, that there was no parallelism between the staining capacity, the toxicity, the production of electric discharge, and the surface tension. The toxicity was measured by the action on tadpoles, the discharge effect by the method of electrocataphoresis, and the surface tension by a Traube stalagmometer. For experiments on the staining capacity infusoria were chiefly employed. The opalines of the frog's intestine were stained by all descriptions of basic and acid dyes. S. B. S.

The Variation of Certain Physical Properties of Cow's Milk with the Subdivision of its Disperse Phases. GEORG WIEGNER (*Kolloid. Zeitsch.*, 1914, **15**, 105—123).—A comparison has been made of the physical properties of ordinary cow's milk with those of the same milk, in which by homogenisation the average diameter of the fat particles was reduced from about 2·9 μ to about 0·27 μ. This change in the degree of dispersity of the fat has no appreciable influence on the density of the milk. Measurements of the viscosity by means of Ostwald's viscometer, which under certain conditions was found to give quite satisfactory results, show that the reduction in the size of the fat particles is accompanied by an increase in the viscosity. This change in viscosity is attributed to the greater adsorption of casein by the fat particles in the homogenised milk in consequence of the much more extensive surface which the particles present in the more highly disperse condition. From the observed change in the viscosity, the author calculates that the thickness of the adsorption envelope surrounding the particles of fat is about 6—7 $\mu\mu$, from which it follows that about 2% of the casein in normal milk is adsorbed, whilst the casein adsorbed by the fat in homogenised milk amounts to about 25%.

The change in the dispersity of the fat has no appreciable influence on the electrical conductivity of the milk, nor, according to freezing-point determinations, on the osmotic pressure. It would therefore seem that the homogenisation produces no change in the distribution of the molecular disperse constituents of the milk.

When kept at low temperature for some time, it is probable that a change takes place in the state of aggregation of the fat particles. On comparing the viscosity of samples of milk which were kept at 42° and 3° for some time previous to the measurements, it was found that the viscosity of the cooled sample at 15° was considerably greater than that of the milk stored at the higher temperature.

Some observations are also recorded in reference to the viscosity of skim milk. The small size of the casein particles precludes the possibility of a change in the degree of dispersity by mechanical means, but such change is doubtless effected by the addition of electrolytes. On addition of potassium hydroxide to fat-free milk, the viscosity increases rapidly with the concentration of the alkali. In similar experiments with acetic acid it was found that the viscosity of the fat-free milk at first diminishes, and afterwards increases rapidly. Reference is made to the bearing of these results on the practice of butter-making. H. M. D.

Chemical Investigations on the Coagulation of Milk and on the Solubility of the Clot in Brine. ORLA-JENSEN, BETZY MEYER, and ANNA D. ORLA-JENSEN (*Zeitsch. physiol. Chem.*, 1914, **93**, 283—306).—When the caseinogen of milk (as distinguished from pure solutions of dicalcium caseinogenate) is only precipitated in the warm by calcium chloride, this behaviour is to be ascribed to the quantities of citrates (and possibly of other salts) contained in the milk. The decomposition of protein caused by rennet does not increase the formaldehyde titre of the milk. At 35° acid begins to coagulate milk before the caseinogen has lost all its calcium. The so-called acid coagulation at higher temperatures is more probably due to calcium salts. Calcium caseinogenates and caseinates form clear solutions with brine, being converted into sodium caseinogenates. The soluble calcium salts present in milk prevent the solution of dicalcium salts, so that in this case only monocalcium caseinogenate and caseinate dissolve. R. V. S.

The Action of Hydrochloric Acid on the Excretion of Alkalis. RIZZARDO SECCHI (*Biochem. Zeitsch.*, 1914, **67**, 143—152).—The administration of hydrochloric acid to dogs receiving a diet consisting chiefly of animal food leads to an increased output of ammonia, potassium, and sodium in the urine. In the case of the last two substances, the increased output is only transient, but it lasts for some time in the case of the ammonia. The calcium and magnesium excreted in the urine are not markedly influenced, but that in the fæces is largely increased, especially the calcium. If sufficient calcium salts are not added to the diet, the administration of the acid can lead to elimination of calcium from the tissues. Hydrochloric acid, when given to rabbits fed on a fresh-cabbage diet which is rich in calcium salts, causes a marked increase in the calcium and magnesium output in the urine, and a smaller increase in the sodium and potassium; the ammonia output is scarcely affected. The calcium excreted in the fæces is also increased, but not to so marked an extent as that in the urine. In the case of man, the effect of hydrochloric acid administration is similar to that produced in the dog. S. B. S.

Ethereal Sulphates [in Urine]. MAX FEDERER (*Zeitsch. physiol. Chem.*, 1914, **92**, 297—301).—The ratio of total sulphate to ethereal sulphate in the urine rises from 4·5 : 1 to 15·2 : 1 when the diet

of rabbits is changed from carrots to cabbage. This is due to an increased elimination of inorganic sulphate arising from the comparatively large amount of sulphur compounds in the cabbage. The ethereal sulphate is only slightly increased, and the nitrogen output is unaltered by the change of food.

Contrary to anticipation, the simultaneous administration of phenol to cabbage-fed rabbits scarcely affects the amount of ethereal sulphate eliminated in the urine, whereas in the case of carrot-fed rabbits, the ethereal sulphate elimination is increased threefold.

H. W. B.

Do the Isomerides of the Cresols "Urogol" or "Urogon" Occur in Urine? C. NEUBERG and L. CZAPSKI (*Biochem. Zeitsch.*, 1914, **67**, 28—31).—Mooser (A., 1909, ii, 1040) has described a substance urogon from cow's urine which is stated to be of ketonic character, and yields on treatment with potassium hydroxide solution a hydrocarbon, $C_{21}H_{42}$, and an isomeride of cresol, C_7H_8O, designated *urogol*. The urogon was obtained by extracting a distillate made slightly alkaline with potassium hydroxide with light petroleum. The authors now show that phenol and cresol can be extracted from distinctly alkaline solutions with light petroleum, and their experiments throw great doubt on the existence of "urogon." They believe that "urogol" is only impure *p*-cresol.

S. B. S.

Non-existence of "Uroleucic Acid." ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1914, **93**, 307—315).—The existence of this substance, originally described by Kirk (A., 1888, 1121), has repeatedly been questioned, and the chief outstanding argument for the occurrence of such a substance is the work of Huppert (A., 1897, i, 576). The author has failed to find the substance in a case of alcaptonuria, and on examination of Huppert's actual preparations finds that they consist of pure homogentisinic acid, as verified by combustion and m. p. The cause of the m. p. given by Huppert is unexplained.

R. V. S.

The Calcium and Magnesium Metabolism in Hyperchlorhydria. RIZZARDO SECCHI (*Biochem. Zeitsch.*, 1914, **67**, 153—162).—The calcium and magnesium metabolism was investigated in a certain number of normal cases, and compared with the metabolism of four patients with hyperchlorhydria. In two of the latter there was an increased calcium output. The clinical significance of the calcium metabolism in these cases is discussed.

S. B. S.

The Distribution and Fate of Colloidal Silver in the Mammalian Body. III. J. VOIGT (*Biochem. Zeitsch.*, 1915, **68**, 477—509).—A detailed description is given of the histological appearance of the organs of rabbits after injection of collargol. The sections were examined stained and unstained, and by both light and dark background illumination. For the latter, the ultramicroscope was employed.

S. B. S.

Comparative Pharmacodynamical Action of Gold in the Colloidal State and in the Form of a Soluble Salt. H. Busquet (*Compt. rend.*, 1915, **160**, 404—406).—The author has compared the action of blue colloidal gold, prepared by chemical methods, and of gold chloride in solution containing the same proportion of metal on (1) the isolated heart of the rabbit, (2) a chloralosed dog. On the isolated heart of the rabbit, colloidal gold, 0·15 gram per litre in Ringer-Locke solution, produces a very marked cardiotonic effect, whilst gold chloride in the same strength solution stops the coronary circulation, and very materially modifies the heart's action. In the case of the dog, 0·003—0·005 gram of colloidal gold per kilogram live weight diminished the frequency of the heart-beats, increased their amplitude considerably, and raised the maximum arterial pressure. Gold chloride, with the same dose, accelerated the heart-beats, diminished the amplitude, produced a fall in arterial pressure, and often stopped the heart's action, causing immediate death.

W. G.

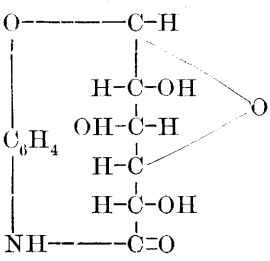
The Physiological Action of Scillitin and Scillidiuretin. W. Kopaczewski (*Biochem. Zeitsch.*, 1914, **66**, 501—508).—The pharmacological action of two substances which have been isolated by the author from squills (A., 1914, i, 913) is described. Scillitin, which is apparently a glucoside, is toxic to rats in the dose of 1 mg. per kilo. of body-weight. Scillidiuretin is relatively non-toxic, and exerts a marked diuretic action when administered to rabbits.

S. B. S.

The Physiological Action of Certain Proteinogenic Amines. Fr. Vanysek (*Biochem. Zeitsch.*, 1914, **67**, 221—231).—Histamine is one of the most powerful restorative substances for the intestine and a strong antagonist to chloroform. It readily disposes of the action of magnesium chloride. Calcium chloride stimulates the circular muscular coat of the small intestine of a cat, but paralyses the longitudinal muscles. An intestine after excitation by histamine is stimulated by calcium, but inhibited by magnesium. Hormonal acts in many respects like histamine, and probably owes its action to this substance. Glycylhistamine has a weaker action than histamine, a fact probably due to the action of glycine as a sympathetic stimulus. Tyramine stimulates the small intestine of the rabbit, stimulates and then inhibits that of the cat, but only inhibits that of the dog. Skin extracts contain two substances with antagonistic actions. The substance which excites the intestine is readily isolated, and is stable when heated. S. B. S.

Behaviour of Phenylhydroxylamine and its Nitroso-derivative in the Body. E. Sieburg (*Zeitsch. physiol. Chem.*, 1914, **92**, 331—339).—After the administration to a dog of a gram of cupferron (ammonium salt of nitrosophenylhydroxylamine) on three successive days, the urine was found to contain albumin and a new glycuronic acid compound, $C_{12}H_{13}O_6N$, which crystallises from dilute alcohol in long needles, arranged in tufts. It has m. p.

179—180° (decomp.) and $\alpha_D^{22} -1{\cdot}56°$. The presence of glycuronic acid is indicated by the orcinol, phloroglucinol, and naphtharesorcinol tests, and after hydrolysis, ether extracts a compound which is recognised by its m. p., 183°, violet colour with ferric chloride, positive indophenol reaction, etc., as *p*-aminophenol. The new compound is readily hydrolysed by emulsin into its two components, denoting the presence of a linking associated with β-glucosides. The compound is therefore the *lactam* of *p-aminophenolglycuronic acid*, and the annexed structure is assigned to it.



Contrary to expectation, phenylhydroxylamine is very much more toxic for rabbits than its nitroso-derivative. After the continued administration of small quantities of the substance, however, traces of the above lactam of *p*-aminophenolglycuronic acid were detected in the urine. H. W. B.

The Influence of the Subsidiary Alkaloids of Opium on the Action of Morphine. R. Meissner (*Biochem. Zeitsch.*, 1914. **67**, 502—503. Compare A., 1913, i, 1279).—Polemical. Reply to Straub (A., 1914, i, 114). S. B. S.

The Fate of Papaverine in the Animal Organism. Kurt Zahn (*Biochem. Zeitsch.*, 1915, **68**, 444—476).—After subcutaneous administration of papaverine to rabbits, cats, and dogs, none of the drug is to be found either in the organs or excreta. Digestion experiments of the alkaloid with single organs lead to no positive result as to the position where it is destroyed. The oxidation and scission products of papaverine, such as veratric acid, and derivatives such as the sulphonate and glycuronate, could not be detected in the organs or excreta. The relationship between the conjugated and free sulphates in the urine was not altered by papaverine injections. The only alteration produced in the urine was the production of a small amount of reducing substance after it had been heated with sulphuric acid. After administration *per os* of a toxic dose, considerable amounts of papaverine were found in the stomach and intestine. The toxic dose for rabbits is more than 0·25 gram per kilo. of body-weight, and amounts of 0·12 gram are indifferent. Cats and dogs are much more sensitive, half this dose producing marked symptoms of intoxication; 0·12 gram is lethal for dogs. Papaverinesulphonic acid is practically non-toxic, and about 35% is excreted unchanged. The papaverine was estimated in the organs by extraction with ammoniacal alcohol, and weighed as free base, which was precipitated from aqueous solutions by ammonia. S. B. S.

The Antigenic Properties of Animal Proteins. Gottlieb Salus (*Biochem. Zeitsch*, 1914, **67**, 357—363).—As regards antigenic properties, the animal proteins may be divided into the following

classes: I, Specific for organ and species (erythrocytes and spermatozoa). II, Specific for species only (blood serum, egg-white, and yolk). III, Not specific for species. This class includes (*a*) those specific for the organ (crystalline lens), (*b*) those with limited specificity for the organ (uvea), (*c*) those which act as antigens, but which are neither specific for the organs nor for species (plasma of the organs). IV, Substances which have no antigenic properties (gelatin and degraded proteins). In the present communication it is shown that leucocytes belong to class I, whilst lymph belongs to class II. S. B. S.

The Sensitising Action of the Porphyrins. WALTHER HAUSMANN (*Biochem. Zeitsch.*, 1914, **67**, 309—317).—It is possible to produce in white mice which have been sensitised by hæmatoporphyrin injections, a deep narcosis in a few minutes after exposure to intense light; the results of this "light stroke" are fatal. The effects of sensitisation on exposure to light are immediate without any incubation time. The chronic forms of sensitisation can be demonstrated by exposure of the animals to the rays of a quartz lamp. A short exposure to the quartz lamp, such as in ordinary circumstances is harmless, produces in sensitised animals necrosis. Mesoporphyrin exerts a photodynamic action on paramæcia and erythrocytes. The sensitising action of hæmatoporphyrin, mesoporphyrin, and phylloporphyrin (with this substance experiments have only been carried out on the blood corpuscles) can be demonstrated on paramæcia and erythrocytes. S. B. S.

The Non-reciprocal Character of the Antagonism between Anions and Cations. JACQUES LOEB (*Biochem. Zeitsch.*, 1914, **66**, 277—288).—The experiments were carried out with *Fundulus*. It was found that the toxic action of certain anions, both organic and inorganic, could be antagonised by the bivalent cations magnesium and calcium. On the other hand, the toxic action of certain cations, such as magnesium, calcium, potassium, lithium, and ammonium, which is exerted when the concentration is sufficiently high, could not be antagonised (except perhaps to a very minute degree) by anions. The non-reciprocal antagonistic actions could also be demonstrated when the anions and cations were in the same salt. Thus calcium nitrate, bromide, etc., were less toxic than the corresponding salts, whilst, on the other hand, the sulphates of toxic cations are not more toxic than the corresponding chlorides. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

The Enzymes of Bacillus Delbrücki. Hans Euler and Harald Cramér (*Biochem. Zeitsch.*, 1914, **67**, 203—208).—*B. Delbrücki* possesses the capacity of inverting sucrose, which capacity is increased to more than 100% when the cells undergo a preliminary

treatment with nutrient solutions containing sugar. This enzyme formation takes place in solutions containing either lactose or dextrose, and quantitatively to the same extent, although in solutions containing the former sugar there is very little growth of the organism. S. B. S.

The Increase of Bacillus Delbrucki in Nutrient Media Containing Lactose or Dextrose. Bj. Palm (*Biochem. Zeitsch.*, 1914, **67**, 209—220).—An account is given of the technique used for determining the number of bacteria formed in the solutions employed by Euler and Cramér in their researches on the enzymes of this bacterium. A modification of Koch's plating method was the principal one employed. S. B. S.

The Action of Alcohol and Osmium on the Combining Groups of Bacteria. Margarete Thorsch (*Biochem. Zeitsch.*, 1914, **66**, 486—500).—Bacteria after treatment with alcohol and osmium react specifically with the agglutins and the complement-binding anti-bodies. Whereas bacteria, after treatment with alcohol, fix the complement in the specific manner after they have been treated with the immune serum, this is not the case with bacteria which have been treated with osmium. The bacteria after treatment with either alcohol or osmium can still act as antigens. S. B. S.

The Formation of Thiosulphuric and Sulphuric Acids from Ethereal Sulphates and Sulphonic Acids. Carl Neuberg and Olga Rubin (*Biochem. Zeitsch.*, 1914, **67**, 82—89).—The following substances were submitted to the action of putrefying bacteria—the sodium salt of chondroitinsulphuric acid, taurine, and potassium ethyl sulphate. As a result, definite amounts of sulphuric acid as a consequence of the putrefactive process could only be detected in the case of the first-named substance; both taurine and chondroitinsulphuric acid gave rise also to thiosulphuric acid, the amounts formed being estimated by Salkowski's method. S. B. S.

The Behaviour of α-Keto-acids towards Micro-organisms. I. Putrefactive Decomposition of Pyruvic and Oxalacetic Acids. Carl Neuberg [with J. Jamakawa] (*Biochem. Zeitsch.*, 1914, **67**, 90—101).—The sodium salts were submitted to putrefaction by the addition to the solution of small amounts of putrefied meat with the necessary nutrient salts and ammonium sulphate and potassium nitrate as sources of nitrogen. The chief product produced both from pyruvic and oxalacetic acids was acetic acid, and not acetaldehyde, as is obtained from these acids by yeast. In addition, formic acid, the amounts of which varied considerably in different experiments, hydrogen and carbon dioxide were also formed. Small amounts of methane were detected in the gaseous products. S. B. S.

The Behaviour of α-Keto-acids towards Micro-organisms. II. The Putrefaction of α-Ketobutyric Acid. Carl Neuberg [with J. Jamakawa] (*Biochem. Zeitsch.*, 1914, **67**, 122—126).—Just as

pyruvic acid yields acetic acid as a putrefaction product, α-ketobutyric acid yields propionic acid. The yield is, however, relatively small (20% of the theoretical), and formic acid, carbon dioxide, and hydrogen are also products of the action. The *m*-phenylhydrazone of α-ketobutyric acid, $C_{10}H_{11}O_4N_3$, melts at 189—190°. S. B. S.

Simultaneous Changes in the Amounts of Glycogen, Nitrogen, and Enzyme in Living Yeast. Sixten Kullberg (*Zeitsch. physiol. Chem.*, 1914, **92**, 340—359).—The author has estimated the amounts of glycogen, nitrogen, and invertase in yeast cells under various conditions. When grown in a nutrient medium containing 2% sugar, the amounts of glycogen and nitrogen in the yeast vary more or less inversely, but a definite relation is not established. On repeated transference of the yeast cells to fresh nutrient media, the amount of glycogen first falls and then increases until it reaches a maximum of about 28%, calculated on the dried yeast. As the glycogen falls, the nitrogen rises, and vice-versa, but again definite proportionality is not observed in these conditions. The amount of invertase in the yeast runs parallel to the nitrogen content.

In a nitrogen-free medium, the glycogen varies as already described, but the nitrogen-content of the yeast steadily falls. On returning the yeast to the nitrogenous medium, the nitrogen-content of the yeast quickly returns to its former level.

In some cases, the preliminary drop in the amount of glycogen does not occur. Increasing the percentage of sugar in the medium leads to a more rapid growth of glycogen in the yeast. H. W. B.

Simultaneous Alteration in the Amounts of Glycogen, Nitrogen, and Enzymes in Yeast. E. Salkowski (*Zeitsch. physiol. Chem.*, 1914, **93**, 336—338).—Polemical. A reply to an observation of Kullberg (preceding abstract). R. V. S.

The Carboxylase in the Juice of Top Yeasts. C. Neuberg and L. Czapski (*Biochem. Zeitsch.*, 1914, **67**, 9—11).—It is possible to prepare from top yeasts a juice containing a carboxylase which will act both on pyruvic and oxalacetic acids. In the experiments, a commercial dried yeast known as "Florylin" was employed. S. B. S.

Phytochemical Reductions. IX. The Conversion of Thiosulphate into Hydrogen Sulphide and Sulphite by Yeast. Carl Neuberg and Ernst Welde (*Biochem. Zeitsch.*, 1914, **67**, 111—118).—When sodium thiosulphate is added to a yeast-sugar fermentation mixture, it undergoes reduction, yielding hydrogen sulphide and sodium sulphite according to the equation:

$$Na_2S_2O_3 + H_2 = H_2S + Na_2SO_3.$$

Up to 15% of the amount of hydrogen sulphide required by this equation was obtained. S. B. S.

Phytochemical Reductions. VIII. The Conversion of Formaldehyde into Methyl Alcohol. Carl Neuberg and Ernst Welde (*Biochem. Zeitsch.*, 1914, **67**, 104—110).—The formation of

methyl alcohol from formaldehyde when the latter is added to a fermentation mixture of sugar and yeast is confirmed. A yield of about 15% was obtained, the methyl alcohol being estimated in the mixture of methyl and ethyl alcohols by oxidation and colorimetric determination of the formaldehyde formed by the methods of Trillat and Grosse-Bohle. The reduction of the aldehyde to the alcohol appears to take place only in the presence of the living yeast. S. B. S.

The Formation of Acetaldehyde in Yeast Fermentation. C. NEUBERG and JOH. KERB (*Ber.*, 1914, **47**, 2730—2732).—The authors re-affirm that acetaldehyde is never a primary product in alcoholic fermentation, although it may be found after such fermentation, in which case it may arise from atmospheric oxidation of the alcohol or from autolysis of the yeast (compare Kostytschev, A., 1912, ii, 589; 1913, i, 323; Buchner, Langheld, and Skraup, *Ber.*, 1914, **47**, 2550; Neuberg and Kerb, A., 1914, i, 118, 1035). D. F. T.

Alcoholic Fermentation. VII. Action of Yeast on Acetaldehyde under Various Conditions. S. KOSTYTSCHEV (*Zeitsch. physiol. Chem.*, 1914, **92**, 402—415. Compare A., 1914, i, 635).—The author finds that the formation of alcohol from acetaldehyde by yeast does not always take place in accordance with the Cannizzaro reaction, because, under certain conditions, the corresponding amount of acetic acid is not produced. Only traces of acetic acid are formed when the transformation of the aldehyde into alcohol is effected by air-dried yeast or by hefanol. Also by the addition of formic acid, but not of formates, the yield of alcohol is increased, whilst the amount of acetic acid is diminished. The former conclusion (*loc. cit.*) is therefore modified by the admission that the reduction of acetaldehyde to alcohol by yeast occurs in other ways besides that expressed by Cannizzaro's reaction. H. W. B.

Phytochemical Reductions. VII. The Enzymatic Conversion of Thioacetaldehyde into Ethyl Mercaptan. C. NEUBERG and F. F. NORD (*Biochem. Zeitsch.*, 1914. **67**, 46—50).—The authors, who have succeeded in carrying out this reaction in fermentation mixtures of sugar with living yeast, find now that the same result can be attained when maceration juice is employed, although the reaction is not so vigorous. As source of thioacetaldehyde they employed thialdin, which readily undergoes scission into thioacetaldehyde and aldehyde-ammonia. S. B. S.

The Valeraldehyde and Amyl Alcohol Fermentation of Methylethylpyruvic Acid. C. NEUBERG and W. H. PETERSON (*Biochem. Zeitsch.*, 1914, **67**, 32—45).—Methylethylpyruvic acid is a probable intermediate product formed when amyl alcohol is produced from *iso*leucine in yeast fermentation. It was therefore of interest to investigate the action of yeast on this product. Both

yeast and maceration juice readily act on it, and produce, by the ordinary carboxylase reaction, α-methylbutaldehyde,

$$CHMeEt\cdot CHO.$$

The chief reaction product, however, was the corresponding amyl alcohol, which was obtained in an optically active form, containing about 30% of the ordinary *d*-alcohol of fusel oil. The residual pyruvic acid, which was unacted on, was found to be optically active, and it is assumed, therefore, that one of the optically active pyruvic acids contained in the racemic, synthetically prepared product was acted on more rapidly than the other. The valeraldehyde was also optically active. The first phase of the carboxylase action is, therefore, the production of an aldehyde, the *d*-form being produced more rapidly than the other. This then undergoes reduction to the corresponding *d*-alcohol. In addition, *d*-valeric acid, and more complex products of aldol character, were produced in the fermentation. Attention is called to the fact that with the exception of the production of an α-keto-acid, all stages in the conversion of *iso*leucine into amyl alcohol can be followed when a cell-free fermentative agent is employed.

Methylethylpyruvic acid [*α-Keto-β-methylvaleric acid*],

$$CHMeEt\cdot CO\cdot CO_2H,$$

prepared by a modification of the process of Mebus, forms a leafly, white mass, m. p. 30°, b. p. 70—75°/11 mm. The *phenylhydrazone* forms yellowish-white needles, m. p. 132—133°. S. B. S.

I. The Reduction of Cinnamaldehyde by Yeast. II. The Fermentation of Benzylpyruvic Acid. Elisabeth Róna (*Biochem. Zeitsch.*, 1914, **67**, 137—142).—I. Cinnamaldehyde, when added to a yeast–sugar fermentation mixture, is reduced to the corresponding alcohol. The latter was found to be optically active. Probably γ-phenylpropyl alcohol is also obtained, but it was not isolated in a pure condition.

II. Benzylpyruvic acid is degraded by yeast in the same manner as pyruvic acid, and yields phenylpropaldehyde. S. B. S.

The Reductase of Yeast. Sergius Lvov (*Biochem. Zeitsch.*, 1914, **66**, 440—466).—The relationship between the amount of methylene-blue reduced, and the amount of carbon dioxide evolved under various conditions of fermentation, was investigated. The course of the reaction was ascertained by removing definite proportions of the fermentation mixture and titrating with titanium chloride to determine the amount of methylene-blue reduced. It was found that for every two molecules of phosphate added to the fermentation mixture, one additional molecular equivalent of methylene-blue was reduced. This result appears to indicate that the phosphate, probably in the form of an organic compound, plays an important part in the reduction process. It is suggested that the withdrawal of two atoms of hydrogen from the fermentation mixture under the influence of the reductase converts the complex organic phosphorus compounds, to which the reduction is

due, into another product, which is not in the position to bring about reduction. According to earlier experiments by the author, the withdrawal of two hydrogen atoms (by methylene-blue) brings about the diminution in the production of two molecular equivalents of carbon dioxide and alcohol in a fermentation mixture. This phenomenon is somehow connected with the phosphate present and the equations of Harden and Young. It is not yet decided which organic phosphorus compound acts as the reducing agent, whether it is the primary compound which is formed in the fermentation mixture before the conversion of the hexose into alcohol and carbon dioxide, or the secondary product, the hexose phosphate. The addition of sugar in the experiments with dried yeast causes in the first hours of fermentation a doubling of the amount of reduction, which was not observed when maceration juice was employed. The probable explanation of this fact is the presence of free phosphates in the maceration juice and their absence in the dried yeast. The experiments indicate generally the importance of the reductase in the fermentation process. The two factors, which are necessary for fermentation, and which are removed by dialysis or washing of the yeast, are also necessary for the reduction process. S. B. S.

Invertase. III. The Influence of Temperature on the Invertase Content of Yeast. J. MEISSENHEIMER and L. SEMPER (*Biochem. Zeitsch.*, 1914, **67**, 364—381).—It is shown that the temperature plays an important part in the enrichment of the invertase in yeast when the organism is allowed to grow in sugar solutions. After twenty-four hours in the beer mash at 25°, the invertase-content is increased four- to five-fold. The optimal temperature for the increase in the mash is about 30°, but in pure sugar solutions it is about 25°. A similar increase is not observed when the yeast is kept in water at 25°, nor is it observed to any extent when kept in sugar solutions at low temperatures. The increase in invertase-content is more or less independent of the strength of the sugar solution, and is thus independent of the growth of the organism. The yeast grown on lævulose showed a larger increase in the invertase than that grown on dextrose.
S. B. S.

Pyruvic Acid as Activating Substance in Alcoholic Fermentation. MAX OPPENHEIMER (*Zeitsch. physiol. Chem.*, 1914, **93**, 235—261).—The fermentation of dextrose by yeast juice at room temperature or at 28° is accelerated very greatly by the addition of alkali pyruvate. The effect is greatest when 0·1% of pyruvate (calculated on the yeast juice taken) is added, and the acceleration may amount to several hundreds per cent. Free pyruvic acid retards fermentation at first, then accelerates it as much as 50%, the maximum effect being obtained by the addition of 1%. In contradiction to the observations of others, the author finds that free pyruvic acid is readily fermented by yeast juice; the evolution of carbon dioxide exceeds that obtained with equal amounts of

pyruvate and dextrose. This makes it improbable that free pyruvic acid should act unfavourably on the enzyme.

The fermentation of dextrose is also, but to a much smaller degree, stimulated by acetaldehyde (optimum 0·005%-.

The fermentation of dihydroxyacetone is also accelerated by alkali pyruvate, but only to a small extent.

An acceleration of the fermentation of glyceraldehyde by pyruvate was not observable with certainty.

The fermentation of lactic acid by yeast juice (which cannot be detected otherwise) takes place after addition of pyruvic acid or its salts. R. V. S.

The Influence of Certain Acids of Biological Importance (Pyruvic, Lactic, Malic, and Tartaric Acids) on the Fermentation of Dextrose. C. NEUBERG and L. CZAPSKI (*Biochem. Zeitsch.*, 1914, **67**, 51—55).—The inhibitory action of the above acids on fermentation of the sugar with various races of yeast was investigated. The inhibitory action is in all cases less than that of acetic acid. S. B. S.

The Ferments of Rum. E. KAYSER (*Compt. rend.*, 1915, **160**, 408—411. Compare Kayser and Demolon, A., 1907, ii, 714).—The author has examined the action of bottom yeast and *Schizosaccharomyces*, used in the manufacture of rum, on molasses must under varying conditions. These two yeasts differ considerably in the amounts of alcohol, volatile acids, and esters they produce, the differences being increased by the addition of bad wine. The addition of mineral or amide nitrogen increases the yield of alcohol and diminishes the amount of volatile acids in the case of the *Schizosaccharomyces*, the reverse being true for bottom yeast. The presence of a microbe found in the molasses doubles the non-alcohol-coefficient in the action of bottom yeast on the molasses must, producing at the same time a high volatile acidity and a feeble yield of aldehyde. The addition of bad wine, yeast extract, or leucine increases the non-alcohol-coefficient, whilst dilution of the must diminishes it, but these two factors are controlled most by the race of yeast employed. The addition of a "levure à voile" increases all the non-alcohol products, notably the esters. W. G.

Formation of Lactic Acid in Alcoholic Fermentation. II. MAX OPPENHEIMER (*Zeitsch. physiol. Chem.*, 1914, **93**, 262—269).—Polemical. A reply to Neuberg and Kerb (A., 1914, i, 785). R. V. S.

The Differences in the Behaviour of Carboxylase and Zymase toward Antiseptics. C. NEUBERG and N. IVANOV (*Biochem. Zeitsch*, 1914, **67**, 1—8).—Whereas the fermentative power of maceration juice as regards sucrose or dextrose is very readily destroyed by the presence of antiseptics, this is not the case as regards pyruvic acid. This statement was confirmed by the investigation of the fermentative power in the presence of the following

antiseptics: sodium fluoride, mercuric chloride, formaldehyde, phenol, and thymol. The carboxylase action of a juice can, by the addition of antiseptics, be demonstrated in the presence of sugars. S. B. S.

The Fermentative Action of Fresh Yeasts in the Presence of Antiseptics. C. Neuberg and F. F. Nord (*Biochem. Zeitsch.*, 1914, **67**, 12—17).—In the case of active yeasts, the addition of toluene does not destroy the fermentative power of sugars. This is much more readily accomplished by chloroform, which acts as a powerful inhibitor of the fermentation of sugar. S. B. S.

Chemical Means of Separating Life and Fermenting Power. Th. Bokorny (*Bied. Zentr.*, 1915, **44**, 137—138; from *Allgem. Brauer- u. Hopfenzeit.*, 1913, 53).—Indications were obtained that the zymase of yeast cells is more resistant to poisons than the plasma.

In 0·1—0·5% sulphuric acid yeast cells are killed, but not the zymase. Similar results were obtained with 1% iron sulphate. Potassium chlorate (2—5%) inhibits growth, but not fermentation. Separation of life and fermenting power was also obtained with ammonium fluoride (1—0·1%), potassium and ammonium oxalates (1—0·1%), and formaldehyde (0·1%). N. H. J. M.

The Behaviour of Yeasts and Moulds towards Nitrates. I. Alexander Kossowicz (*Biochem. Zeitsch.*, 1914, **67**, 400—419).—Various moulds and yeasts were grown on different culture media containing nitrate as a source of nitrogen. After varying intervals the culture media were tested for the presence of nitrites and ammonia. The results, which do not admit of any summarisation, are tabulated. S. B. S.

The Assimilation of Carbon and Nitrogen by Moulds. Alexander Kossowicz (*Biochem. Zeitsch.*, 1914, **67**, 391—399).—Ten different moulds were employed, and were grown on nutrient media containing the necessary salts. When carbamide was used as a source of carbon, development did not take place; on the other hand, when employed as a source of nitrogen in a medium containing sucrose or mannitol as a source of carbon, development took place. Uric acid and hippuric acid would serve as sources both of nitrogen and carbon. So also could glycine and guanine. Guanidine, on the other hand, could serve only as a source of nitrogen. Potassium thiocyanate could serve as a source of nitrogen only, but no very vigorous development took place. Nitrites, nitrates, and calcium nitride could act as sources of nitrogen. S. B. S.

Action of Moulds on the Amount of Alkaloid in Opium. Oscar von Friedrichs (*Zeitsch. physiol. Chem.*, 1914, **93**, 276—282). —*Penicillium viridicatum* and *Citromyces glaber* do not attack the opium alkaloids. *Aspergillus niger* attacks narcotine and codeine,

but not morphine, whilst *A. Ostianus* (found on Levant opium) appears to destroy this alkaloid also, but very slightly. R. V. S.

Constituents and [Physiological] Actions of Lupin Seeds. GUSTAV MUENK (*Landw. Versuchs.-Stat.*, 1914, **85**, 393—416).—In addition to other enzymes previously known, lupin seeds contain an enzyme which produces lactic acid from starch and from several sugars. Blue lupin seeds also contain a non-poisonous, agglutinising enzyme, which when heated at 70—75° rapidly becomes inactive, and can, in this manner, readily be distinguished from ricine. N. H. J. M.

The Alcoholic Fermentation of the Higher Plants. A. R. MINENKOV (*Biochem. Zeitsch.*, 1914, **66**, 467—485).—The method is described by means of which the carbon dioxide and alcohol produced by sterilised seeds of *Vicia faba* can be estimated. The seeds were immersed in water through which air was bubbled, and were kept under aseptic conditions in an apparatus which is described and figured. It was ascertained that an alcoholic fermentation of higher plants takes place in the presence of oxygen, which is intimately connected with their vital activity and growth. The factors which diminish growth increase the alcohol production in the presence of air. These factors are too high or too low temperatures, and osmotic pressures produced by the solution in the water surrounding the seeds of both organic and inorganic substances. Absence of oxygen, which diminishes growth, tends to increase the production of alcohol. In inhibition of development of the seeds, the oxidative processes are diminished; such a diminution occurs long before the death of the seeds. S. B. S.

Action of Calcium and Magnesium in the Nutrition of Plants. E. HASELHOFF (*Bied. Zentr.*, 1914, **43**, 619—620; from *Landw. Jahrb.*, 1913, **45**, 609).—The results of pot and field experiments with various plants and with different soils, extending over three years, failed to show any favourable action due to any definite relation of calcium and magnesium applied as carbonate. N. H. J. M.

Action of Chloroform on Chlorophyll Assimilation. K. VON KÖRÖSY (*Zeitsch. physiol. Chem.*, 1914, **93**, 145—153).—The experiments were carried out with a shoot of *Elodea canadensis* immersed in a solution of carbon dioxide, the assimilation being followed by counting the number of bubbles rising in a given time. Chloroform solutions show a narcotic effect at concentrations between 0·004 and 0·009 gram molecules of chlorophyll per litre. R. V. S.

Hydrolysis of Organic Esters of Phosphoric Acid. HANS EULER and BETH EULER (*Zeitsch. physiol. Chem.*, 1914, **92**, 292—296).—Extracts of the green leaves of the maple tree and also of germinating barley grains effect the hydrolysis of the sodium salt of hexosephosphoric acid, and therefore contain phosphatase. The

amount of phosphatase in barley increases as the germination proceeds, reaching a maximum on the fourth day. H. W. B.

Organic Acids from the Sap of the Sugar Maple. Edmund O. von Lippmann (*Ber.*, 1914, **47**, 3094—3095; 1915, **48**, 288).—I. The calcareous product which forms on the walls of the evaporating pans in the manufacture of maple sugar (so-called "sugar sand") was found to contain *d*-tartaric, *l*-malic, and tricarballylic acids.

II. The presence of malic acid in the "sugar sand" of maple sap had already been noticed by Hill (1888) and Warren (A., 1911, ii, 821). J. C. W.

Microchemistry of Hydroxymethylanthraquinone. An Enzyme which Decomposes Anthraglucoside in Rhubarb. R. Wasicky (*Ber. deut. botan. Ges.*, 1915, **33**, 37—45).—Rhubarb plants contain at least two enzymes, an oxydase and an enzyme which decomposes anthraglucoside.

Crystals of hydroxymethylanthraquinone were found in one root, out of several, of *Rumex hymenosepalus*; the root was injured by parasites, which possibly caused the decomposition of the anthraglucoside. In damaged rhubarb rhizomes crystals were found after they had been placed for three to four hours in dilute glycerol; in some undamaged samples, crystals were formed in two days; the amount of crystals produced was, however, much less in the undamaged samples than in those which were injured by moulds or insects. N. H. J. M.

Organic Phosphoric Acid of Wheat. G. Clarke (T., 1915, **107**, 360).—A mixture of complex calcium and magnesium salts of the type $C_{12}H_{22}O_{44}Ca_7Mg$ has been obtained from wheat by extraction with dilute hydrochloric acid. It is similar to the phytin obtained from mustard (T., 1914, **105**, 535), and is decomposed by sulphuric acid into inositol and phosphoric acid. The free inositol phosphoric acid obtained from the calcium magnesium salt gave a strychnine salt crystallising in slender needles, m. p. 218—219°. G. F. M.

Transformations of Starch in Potatoes During Drying. Alida Huizinga and H. J. F. de Vries (*Chem. Weekblad*, 1915, **12**, 268—272).—A repetition of the experiments of Waterman (*Chem. Weekblad*, 1914, **11**, 322) on the effect of drying potatoes at about 40°, has not confirmed his statement that large quantities of sucroses are produced in the process. A large number of samples were examined, and only traces of sucrose were detected. A. J. W.

Plant Ferments. II. The Amylase of Potatoes. G. Doby (*Biochem. Zeitsch.*, 1914, **67**, 166—181).—Amylase is always present in the juice of the resting tuber, but the amount is less than that of cereal seeds. The optimal temperature of its action is 40°,

which is less than many other plant amylases. Sodium fluoride is a good activator. Sodium chloride and mono- and di-potassium phosphates exert an inhibitory action. Potassium nitrate is without action. Hydrogen and hydroxyl ions in small concentrations activate, but in large concentrations inhibit the ferment action. The boiled potatoe juice has also an activating property. Juice which has been filtered through porcelain loses its acitivity. The activity is inhibited by sugars in the following (increasing) order: mannose, galactose and sucrose, arabinose, lævulose and lactose, dextrose and maltose. The scission products of the ferment possess, therefore, the greatest power of inhibiting its activity. The inhibitory action of sugars is discussed by the author in some detail.

S. B. S.

Present Position of Soil Chemistry with Special Reference to the Organic Compounds. S. L. Jodidi (*Landw. Versuchs-Stat.*, 1914, **85**, 359—391).—A summary of the results of recent investigations, in the United States, of the various organic compounds in soils. N. H. J. M.

Characterisation of Soils According to the Molecular Composition of the Silicates Decomposed by Hydrochloric Acid. R. Gans (*Bied. Zentr.*, 1914, **43**, 512—514; from *Int. Mitt. Bodenk.*, 1913, **3**, 527).—The zeolitic silicates in soils, which have been protected from weathering by the presence of carbonates of the alkaline earths, have the characteristic composition of aluminium silicates. When they have been acted on by carbon dioxide they contain less base in relation to alumina; and, when weathered under alkaline conditions, less than 3 mols. SiO_2 to 1 mol. Al_2O_3.

Neutral, alkaline, or acid soils are best characterised by the relation of base to silica and alumina in the extract obtained with strong boiling hydrochloric acid; the percentage amounts of bases extracted cannot be employed as criteria.

It is desirable to estimate the silica by the hydrochloric acid method, and to extend the mol. calculation of the results to the bases not combined with other acids (phosphoric and sulphuric acids, etc.), as in this manner the degree of weathering is shown more sharply than by the silica and alumina alone. The chemical composition of the weathered silicates has, moreover, great influence on the solubility of phosphoric acid and bases, and influences the hygroscopicity, which should also be estimated.

The mol. calculation is also of considerable value when for the complex, resulting from weathering, a physical rather than chemical union is assumed; it is immaterial, for instance, whether an acid reaction is explained by acid aluminate-silicates or by absorptive unsaturated gels of silica and alumina. N. H. J. M.

Mobilisation of the Phosphoric Acid of Soils under the Influence of Bacteria. S. A. Severin (*Bied. Zentr.*, 1914, **43**, 671—672; from *Ber. bakt.-agron Stat. Moscow*, 1913, No. 20).—The results of experiments with *Bacillus radicicola* and *B. pyocyaneus*

showed that with these organisms the oxidation process is similar to that induced by the complex bacterial flora of soil extracts, except as regards the amount of carbon dioxide, which is much less than with the mixed soil bacteria. Oxidation was less with *B. pyocyaneus* than with *B. radicicola*.

The amount of carbon dioxide produced shows no relation to the production of soluble phosphoric acid; and of two organisms which produce about the same amounts of carbon dioxide, the one may increase, whilst the other diminishes, the amount of soluble phosphorus.

The conclusion is drawn that the final result as regards the production of soluble phosphorus in soils does not only depend on the bacterial action on phosphates and the solution of phosphates by carbon dioxide, but also on a series of biochemical phenomena closely connected with the physiological properties of the bacteria.

N. H. J. M.

Vegetation Experiments and Soil Analysis. O. Lemmermann (*Landw. Versuchs-Stat.*, 1914, **85**, 147—154).—Two different soils yielded, in three weeks, carbon dioxide corresponding with 13% and 3·5% respectively of the carbon. When the soils were mixed with sand so that both mixtures contained the same amount of organic matter, the amounts of carbon dioxide produced were 19% and 15%. The different rates of decomposition depended, therefore, on the character of the soils rather than the nature of the organic matter.

As regards the extraction of soils, for estimating solubilities, the best method seems to be continuous percolation of the solvent. This should be possible even with heavy soils, if these are mixed with sand. N. H. J. M.

Action of Hydroxyl Ions on Clays and Clayey Soils. P. Rohland (*Landw. Versuchs-Stat.*, 1914, **85**, 105—108).—A reply to Maschhaupt (A., 1914, i, 470). A correlation exists between the concentration of the OH' ions and the constitution of the clay. Some "fatty" clays scarcely react at all with the hydroxyl ions, whilst others react with very low concentrations. N. H. J. M.

The Colloid Properties of Terra rossa. Paul Rohland (*Kolloid. Zeitsch.*, 1914, **15**, 96—98).—The mechanical, physical, and chemical properties of this red clay are supposed to be due to the presence of colloid substances and of silicates which form colloids in contact with water. H. M. D.

Organic Chemistry.

Catalytic Hydrogenation of Liquids Under the Influence of the Common Metals at Moderate Temperatures and Pressure. ANDRÉ BROCHET and MAURICE BAUER (*Bull. Soc. chim.*, 1915, [iv], **17**, 50—55).—The authors have applied the method of hydrogenation by means of reduced nickel, already described (A., 1914, i, 645), to the hydrogenation of a number of compounds having an ethenoid linking, namely, Δ^{α}-octene, cinnamic acid and its derivatives, piperonylacrylic acid, anethole, eugenol, safrole, and *iso*eugenol.

W. G.

Catalytic Hydrogenation of Liquids Under the Influence of the Common Metals at Moderate Temperatures and Pressure. ANDRÉ BROCHET and ANDRÉ CABARET (*Bull. Soc. chim.*, 1915, [iv], **17**, 55—59).—An extension of the work mentioned in the preceding abstract, the hydrogenations being carried out at ordinary pressure.

W. G.

Optical Activity of Petroleum. I. K. TRAUBENBERG (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1043—1048).—The question of the dependence of the optical activity of petroleum on the presence of decomposition products of cholesterol is discussed (compare Marcusson, A., 1907, i, 466; 1908, ii, 394).

The author's experiments show that the dry distillation of cholesterol yields a brown oil and a viscous, fluorescent oil, both containing constituents capable of giving formolites with sulphuric acid and formaldehyde. The ready solubility of these formolites in sulphuric acid, their combination with bromine and their rapid absorption of oxygen indicate their unsaturated character. The results obtained, as well as those of Marcusson, indicate, however, the invalidity of Marcusson's conclusion that the predominant cause of the optical activity of petroleum lies in the presence of the immediate decomposition products of cholesterol (compare Steinkopf and Winternitz, A., 1914, i, 645). The bearing of these results on the origin of petroleum is considered.

T. H. P.

Action of Magnesium on Tribromo*iso*pentane [$\beta\gamma\delta$-Tribromo-γ-methylbutane]: Synthesis of an Open-chain Hydrocarbon, $C_{10}H_{18}$. VL. KRESTINSKI (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 900—908. Compare Krestinski and Krivorotko, A., 1913, i, 1145).—The author has investigated the action in ethereal solution of magnesium on the mixture of $\beta\gamma\delta$-tribromo-γ-methylbutane with a small proportion of $\alpha\beta\gamma$-tribromo-γ-methylbutane obtained by the action of bromine on dimethylethylcarbinol in presence of iron wire on a water-bath (compare Ipatiev and Sviredski, A., 1902, i, 132). The products consist of: (1) *$\gamma\zeta$-Dimethyl-$\Delta^{\beta\xi}$-octadiene*,

$$CHMe{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CHMe,$$

b. p. 153—155°, D_4^{20} 0·7767, n_D^{20} 1·44453, which yields carbon dioxide and succinic and acetic acids on oxidation by means of permanganate, and forms liquid *γζ-dibromo-γζ-dimethyloctane*,

$$CMeEtBr\cdot CH_2\cdot CH_2\cdot CMeEtBr,$$

when treated with hydrogen bromide at −20°; (2) a small proportion of *βη-dimethyl-Δ$^{\beta\zeta}$-octadiene*, $CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CH{:}CMe_2$, b. p. 161—163°, D_4^{20} 0·7849, n_D^{20} 1·44814, which yields succinic and acetic acids on oxidation.

These results, together with those previously obtained by the author and Krivorotko (*loc. cit.*) with tribromo*iso*butane, show that the action of magnesium on 1 : 2 : 3-tribromo-derivatives of saturated hydrocarbons constitutes a general method for obtaining diethylenic hydrocarbons of definite structures, and that the coupling of the hydrocarbon residues takes place between the carbon atoms to which the primary bromine atoms are attached. T. H. P.

Preparation of Hydroxy*iso*propyl Derivatives of Hydrocarbons and Their Derivatives. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 280026; from *J. Soc. Chem. Ind.*, 1915, **34**, 378).—Acetone-sodium is obtained as a very reactive, crystalline substance, readily soluble in ether or light petroleum, by the action of sodium amide on acetone, in the presence of ether, at low temperatures. It replaces one or more atoms of hydrogen, in hydrocarbons or their derivatives, for the group $-CMe_2\cdot OH$. The products are obtained as sodium compounds which can be decomposed by acids. J. C. W.

Preparation of Homologues of Tetramethylene Glycol [*n*-Butane-αδ-diol]. VIT. LONGINOV (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1084—1096).—From the results obtained by Bouveault and Blanc (A., 1905, i, 13) and by Zelinski and Ujedinov (A., 1913, i, 466), it would seem that the loss of a carbethoxyl group on reduction by means of sodium and alcohol is a phenomenon occurring widely with derivatives of ethyl malonate. The author has utilised it for obtaining homologues of αδ-dihydroxy-*n*-butane from esters of tricarboxylic acids of the type $CO_2Et\cdot CR(CO_2Et)\cdot CH_2\cdot CO_2Et$. The corresponding glycols are obtained in this way more economically and in greater yield than by reduction of dibasic acids, there being no possibility of the occurrence of condensation.

The interaction of ethyl sodiomalonate and ethyl chloroacetate yields: (1) ethyl ethane-*aaβ*-tricarboxylate, $CO_2Et\cdot CH_2\cdot CH(CO_2Et)_2$, which is a viscous oil, b. p. 146—148°/11 mm., D_4^{20} 1·0931, and (2) *ethyl propane-αββγ-tetracarboxylate*,

$$CO_2Et\cdot CH_2\cdot C(CO_2Et)_2\cdot CH_2\cdot CO_2Et,$$

which is a transparent, viscous oil, b. p. 187—189°/11 mm.

β-Ethylbutane-αδ-diol, $OH\cdot CH_2\cdot CHEt\cdot CH_2\cdot CH_2\cdot OH$, obtained by reducing ethyl ethane-*aaβ*-tricarboxylate by means of alcohol and excess of sodium at 130—140°, is a colourless, odourless, viscous liquid, b. p. 129—131°/10 mm., D_4^{20} 0·9825, n^{20} 1·4540.

β-Propylbutane-αδ-diol, $OH\cdot CH_2\cdot CHPr^{\alpha}\cdot CH_2\cdot CH_2\cdot OH$, obtained in

an analogous manner, is a colourless, odourless, viscous liquid, b. p. 138—140°/10 mm., D_4^{20} 0·9625, n^{20} 1·4540. Neither this nor the preceding compound solidifies at −20°.

In the homologous series, butane-αδ-diol, β-methylbutane-αδ-diol, β-ethylbutane-αδ-diol, and β-propylbutane-αδ-diol, the specific gravity decreases continuously as the molecular weight increases.

αδ-Dibromo-β-propylbutane, $CH_2Br\cdot CHPr\cdot CH_2\cdot CH_2Br$, prepared by the action of hydrobromic acid on the corresponding diol in a sealed tube, is a liquid, b. p. 103°/9 mm., D_4^{20} 1·5269, n^{20} 1·5018, but was not obtained quite pure. It is accompanied by the corresponding oxide, *3-propyltetrahydrofuran*, $O<\begin{matrix}CH_2\cdot CHPr\\ |\\ CH_2\cdot CH_2\end{matrix}$, which is a colourless, highly volatile liquid, with a pleasant, ethereal odour, b. p. 144°/750 mm., D_4^{20} 0·8618, n^{20} 1·4243; it does not react with bromine, and decolorises permanganate very slowly.

3-Propylpyrrolidine, $NH<\begin{matrix}CH_2\cdot CHPr\\ |\\ CH_2\cdot CH_2\end{matrix}$, obtained as principal product when αδ-dibromo-β-propylbutane is heated in a sealed tube with methyl-alcoholic ammonia at 150°, is a colourless, mobile liquid, b. p. 158—160°/746 mm., D_4^{20} 0·8450, n^{20} 1·4469, with an intense odour recalling that of piperidine; it fumes in the air, absorbing moisture and carbon dioxide, and yields an oily hydrochloride.

When heated with the potassium derivative of phthalimide (2 mols.), αδ-dibromo-β-propylbutane (1 mol.) yields *αδ-diphthalimino-β-propylbutane*, $C_8H_4O_2N\cdot CH_2\cdot CHPr\cdot CH_2\cdot CH_2\cdot C_8H_4O_2N$, m. p. 99—100°, and this, when heated in a sealed tube with fuming hydrochloric acid at 180°, is converted into *αδ-diamino-β-propylbutane* (*β-propylputrescine*) *hydrochloride*, $NH_2\cdot CH_2\cdot CHPr\cdot CH_2\cdot CH_2\cdot NH_2,HCl$, which forms small, hygroscopic crystals, m. p. 247—248°. T. H. P.

Preparation of Di-secondary Glycols. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 277392; from *J. Soc. Chem. Ind.*, 1915, **34**, 303).—These compounds are obtained by the reduction of saturated aliphatic aldehydes in acid media at metallic cathodes. J. C.W.

Action of Concentrated Sulphuric Acid on Acetylene Derivatives. J. S. ZALKIND (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 897—900).—The author has investigated the colour reactions given with concentrated sulphuric acid by acetylenic and saturated γ-glycols (compare Dupont, A., 1914, i, 530) and by certain related compounds, a crystal of the compound or its solution in a few drops of acetone or chloroform being added to 5—6 c.c. of the acid.

Acetylenic γ-glycols give an intense coloration which, with tetramethyl-, tetra-ethyl- and *s*-dimethyldiethyl-butinenediol, is yellowish-red, and with tetraphenylbutinenediol, green changing to yellow. Diphenylbutinenediol in acetone gives a yellowish-red coloration, and *s*-diphenyldimethylbutinenediol in chloroform a greenish-violet colour, and in acetone, a red colour with a slight green fluorescence. The corresponding ethylenic glycols, especially those of the aliphatic series, yield considerably less intense colours. Thus, tetra-methyl- and

tetra-ethyl-butenediol give comparatively pale yellow colorations, and the same is the case with the oxide obtained from dimethyldiethyl-butenediol; of slightly greater intensity is the colour obtained with diphenylbutenediol. Lemon-yellow colorations are given by saturated γ-glycols, by the oxide formed from dimethyldiethylbutanediol, and by the acetyl derivative of diphenylbutanediol.

δ-Phenyl-β-methyl-Δγ-butinen-β-ol (compare Iocitsch, A., 1914, i, 401) gives a yellowish-brown coloration, not less intense than that obtained with acetylenic γ-glycols; the corresponding saturated hydrogenated alcohol, δ-phenyl-β-methylbutan-β-ol, yields only a feeble, lemon-yellow colour. αε-Diphenyl-γ-methyl-$\Delta^{\alpha\delta}$-pentadi-inen-γ-ol (compare Iocitsch, *loc. cit.*) dissolves in concentrated sulphuric acid to a violet solution; with its solution in an oxygen-free solvent the colour obtained is reddish-violet, and when an oxygenated solvent is used, the acid liquid is yellowish-brown in transmitted light and shows bright blue fluorescence in reflected light. The tetrahydrogenated derivative of this alcohol gives no coloration with sulphuric acid. In dilute acetone or chloroform solution, phenylacetylene yields no coloration.

These colour reactions, which are given only with concentrated sulphuric acid and are regarded as examples of halochromy, appear to be more characteristic of certain compounds with triple linkings than of hydroxy-derivatives. T. H. P.

Preparation of Glycerol Halogenhydrins and Esters of Polyhydroxyaliphatic Acids. A. Grün (D.R.-P. 277901; from *J. Soc. Chem. Ind.*, 1915, **34**, 303).—An addition to D.R.-P. 272337 (A., 1914, i, 1048). The reaction between the triglycerides of hydroxy-aliphatic acids and halogen hydracids may be effected under atmospheric pressure. J. C. W.

Preparation of Ethers. Chem. Werke vorm. H. Byk (D.R.-P. 278777; from *J. Soc. Chem. Ind.*, 1915, **34**, 303).—Vaporised alcohols, or ethylene hydrocarbons mixed with water and (or) alcohol, are passed over heated alum, which works as a catalyst at a lower temperature than alumina. Ethyl alcohol or ethylene yields a mixture of ether (25–50%) and alcohol. J. C. W.

Action of Carbon Dioxide on Etherates of Magnesium Alkyl Haloids. A. E. Tschitschibabin (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 800—802).—The observations made by the author and Elgazin (A., 1914, i, 276, 1065) on the replacement of alkyloxyl groups by the radicles of organo-magnesium compounds afford a very simple explanation of the results obtained by Stadnikov and Kuzmina-Aron in their study of the action of carbon dioxide on etherates of magnesium alkyl haloids (A., 1912, i, 971). This action comprises the following series of changes: (1) When a magnesium alkyl haloid is heated with a benzhydryl ether, the alkyloxyl group of the latter is replaced by the alkyl radicle of the organo-magnesium compound, $CHPh_2\cdot O\cdot C_4H_9 + MgPrI = CHPrPh_2 + MgI\cdot O\cdot C_4H_9$. (2) The last compound, like other alkyloxides, then reacts with carbon dioxide, giving $MgI\cdot O\cdot CO\cdot O\cdot C_4H_9$,

and (3) this is decomposed by mineral acids, yielding butyl alcohol and carbon dioxide, $2MgI\cdot O\cdot CO\cdot O\cdot C_4H_9 + 2HCl = MgI_2 + MgCl_2 + 2CO_2 + 2C_4H_9\cdot OH$.

As regards the evidence yielded by Stadnikov's results in support of Grignard's formulæ, the author points out that these results do not refute Tschelincev's observations relating to the different products obtained on decomposing with water the two etherates formed (1) from magnesium amyl iodide and ethyl ether, and (2) from magnesium ethyl iodide and ethyl amyl ether, ("Individual Organo-magnesium Compounds," Moscow, 1908, 126). If no supplementary hypothesis concerning differences in the valencies of the quadrivalent oxygen is introduced, Grignard's formula would indicate that both of these reactions should yield one and the same compound, $C_5H_{11}\cdot OEt_2\cdot MgI$, so that the products of decomposition by water should be identical.

T. H. P.

Etherates of Aluminium Iodide. N. Domanicki (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1078—1082).—In order to obtain the etherate of aluminium iodide in a pure state, the absence of moisture is essential. The author employs a bent tube consisting of two limbs connected by a ground joint and fitted with a cock to admit of evacuation. One limb contains freshly distilled aluminium iodide and the other, thoroughly dried, cooled ethyl ether, which is gradually introduced into the first limb. The *ethyl etherate*, AlI_3,Et_2O, forms colourless or yellow, unstable crystals, m. p. about 49°, and is decomposed by water with vigorous effervescence. If an ethereal solution of the complex is left in an imperfectly closed vessel or if iodine is gradually added to the aluminium shavings beneath the solution, the etherate undergoes transformation into the more stable *compound*, $Al(OH)_3,AlI_3,Et_2O$, which remains unchanged under ether, dissolves in carbon disulphide with separation of aluminium hydroxide, and is decomposed slowly by water; in the air it deliquesces, and, when heated, it decomposes without melting. The formation of this compound would be expected on the assumption that the etherate has the doubled molecular weight in solution, as is the case with aluminium iodide (compare Kohler, A., 1901, ii, 21; Beckmann, A., 1909, ii, 642): $Et_2O,AlI_3,AlI_3,Et_2O + 3H_2O = Al(OH)_3,AlI_3,Et_2O + Et_2O + 3HI$. An analogous compound has been obtained from magnesium iodide ethyl etherate (compare Blaise, A., 1905, i, 111), but is less stable than the latter; also Holroyd (P., 1904, **20**, 38) prepared the compound,

$$4Et_2O,MgBr_2,MgBr\cdot OH.$$

Aluminium bromide etherates, on the other hand, do not appear to yield etherates of the bromo-hydroxide. Other ethers, such as *iso*amyl ether, form etherates of aluminium iodo-hydroxide, but only with difficulty, probably owing to the less pronounced hygroscopicity of the ethers.

With organic compounds of almost all classes, aluminium iodide forms complexes, which are mostly highly unstable and separate as red, yellow or brown precipitates when ethereal solutions of their components are mixed.

The structure of the etherates is best expressed according to Werner's co-ordinated formulæ. T. H. P.

Oxidation of Ether. R. M. Isham and C. E. Vail (*J. Amer. Chem. Soc.*, 1915, **37**, 902—906).—As comparatively little attention has been hitherto devoted to the oxidation of ether, a series of experiments has been carried out on the behaviour of ether vapour when heated with air or oxygen. The results show that acetaldehyde and acetic acid are produced, and that the oxidation begins at about 110° and proceeds rapidly at 160°.

When chromic acid is added to ether, a violent reaction takes place with evolution of acetaldehyde vapour and the separation of green chromic oxide. If the chromic acid is introduced into ether previously cooled to − 10°, a yellow solution is first produced, but oxidation begins almost immediately with the same results as those obtained at the ordinary temperature. E. G.

New Method of Preparation of Dibromomethyl Ether, $(CH_2Br)_2O$, and Dibromo- and Di-iodo-methane. V. E. Tischtschenko and I. L. Rabcevitsch-Zubkovski (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 705—708).—The preparation of dibromomethyl ether in quantity by the passage of hydrogen bromide through dry trioxymethylene occupies a considerable time (compare *ibid.*, 1887, **19**, 472). The pure ether may be obtained in 60% yield by adding red phosphorus, trioxymethylene and bromine gradually, with agitation and cooling, to water, the trioxymethylene being taken in somewhat less than the theoretical quantity:

$$2P + 10Br + 3H_2O + 10CH_2O = 2H_3PO_4 + 5(CH_2Br)_2O.$$

Dibromomethane may be prepared in highly pure condition and in about 60% yield by the action of aluminium bromide on dibromomethyl ether, the mixture being heated gradually to 175—180°. Di-iodomethane may be obtained similarly by heating aluminium iodide and di-iodomethyl ether, $(CH_2I)_2O$, together gradually to 120°.

T. H. P.

Oxonium Compounds of Sulphuric Acid with Ethers. V. V. Tschelincev and N. A. Kozlov (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 708—725).—The investigations of Archibald and McIntosh (T., 1904, **85**, 919), Hantzsch (A., 1908, ii, 14), Oddo and Scandola (A., 1910, ii, 1035), and Pound (T., 1911, **99**, 698) show that sulphuric acid and ethers form compounds, to which, from their analogy to the substituted ammonium sulphates, the authors attribute the structures of oxonium derivatives, $OH\cdot S(:O)_2\cdot O\cdot OHR_2$ and $S(:O)_2(\cdot O\cdot OHR_2)_2$.

The authors' experiments have been made with ethyl and *iso*-amyl ethers. Mixtures in the proportions $H_2SO_4 + R_2O$ and $H_2SO_4 + 2R_2O$ remain unchanged in composition for one to two months. Thermochemical measurements show that the interaction of sulphuric acid with ethers proceeds moderately rapidly, is accompanied by perfectly definite and comparatively large thermal effects, and comes to a sharp end after the introduction of each of the two

molecules of the ether. The amounts of heat generated in Cal. per gram-mol. are: $H_2SO_4 + Et_2O$, 6·83; $H_2SO_4 + O(C_5H_{11})_2$, 6·15; $H_2SO_4,Et_2O + Et_2O$, 1·74; $H_2SO_4,O(C_5H_{11})_2 + O(C_5H_{11})_2$, 1·15. These values are analogous to the following: $H_2SO_4 + H_2O$, 6·38; $H_2SO_4,H_2O + H_2O$, 3·04; $MgPrI + Et_2O$, 6·63. The calorimetric measurements show, further, that no compound of sulphuric acid with ether is formed containing more than 2 mols. of ether per mol. of the acid.

When an aliphatic ether is gradually mixed with sulphuric acid at 20°, neither component undergoes scission and no formation of esters takes place. On the other hand, aromatic ethers and acetals yield, under similar conditions, sulphonic derivatives and esters of sulphuric acid respectively. Cryoscopic measurements in acetic acid show that the compounds of ethers with sulphuric acid either undergo complete decomposition into their components, or are converted into the corresponding compounds of sulphuric and acetic acids, $H_2SO_4,C_2H_4O_2$ and $H_2SO_4,2C_2H_4O_2$. Cryoscopic measurements in phosphoryl chloride show, however, that ethers and sulphuric acid undoubtedly form compounds. At low temperatures these compounds crystallise, the melting points being: H_2SO_4,Et_2O, −66 to −64°; $H_2SO_4,O(C_5H_{11})_2$, −67 to −68°; $H_2SO_4,2Et_2O$, −88°; $H_2SO_4,2O(C_5H_{11})_2$, −74°.

T. H. P.

A Method of Diagnosis of the Monoglycerophosphoric Esters, and the Constitution of Crystalline Sodium Glycerophosphate. L. Grimbert and O. Bailly (*J. Pharm. Chim.*, 1915, [vii], **11**, 153—157).—A detailed account of work already published (this vol., i, 73). W. G.

New General Method for Preparing Mercaptans. B. K. Mereshkovski (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1082—1084).—This method, which gives yields of 50—60%, is based on the reactions expressed by the equations: $3R{\cdot}OH + 3Br + P = 3RBr + H_3PO_3$; $4H_3PO_3 + Na_2SO_4 = Na_2S + 4H_3PO_4$; $Na_2S + H_3PO_4 = Na_2HPO_4 + H_2S$ and $RBr + H_2S = R{\cdot}SH + HBr$.

The alcohol, red phosphorus, moist sodium sulphate and sodium sulphide are introduced into a flask, and, while the contents are kept thoroughly mixed by a motor-driven stirrer, the requisite quantity of bromine is added. The reaction proceeds with considerable development of heat and liberation of hydrogen bromide. The mixture is distilled in a current of steam, mercaptan, alkyl bromide and excess of alcohol being collected. Further purification is conducted in the ordinary manner.

This method is applicable to primary, secondary and tertiary alcohols, and its simplicity, the accessibility of the materials used, and the good yield of mercaptan obtained, render it greatly superior to other known methods. T. H. P.

The Action of Various Acids on Sodium Thiosulphate in the Presence of Formaldehyde. L. Vanino and A. Schinner (*Ber.*, 1914, **47**, 2562—2565).—The view that the formation of

thioform in the interaction of sodium thiosulphate and formaldehyde in aqueous solution is to be referred to the occurrence of a hydroxymethylenethiosulphuric acid, has been expressed by several investigators (Vanino, A., 1902, i, 744; Schmidt, A., 1906, i, 711; 1907, i, 282). It is now shown that the reaction quantitatively follows the course expressed by the equation

$$3OH\cdot SO_2\cdot S\cdot CH_2\cdot OH = (CH_2S)_3 + 3H_2SO_4,$$

but endeavours to isolate the hydroxymethylenethiosulphuric acid were fruitless. Experiment shows that the thioform is not produced by the direct action of formaldehyde on sulphur, or by the interaction of formaldehyde and thiosulphate in the presence of acids such as oxalic or tartaric which are known to decompose thiosulphate with production of hydrogen sulphide. No thioform or sulphur was obtained in the action of formic, acetic, butyric, oxalic, tartaric, trichloroacetic, hydriodic, sulphurous, sulphuric (20%) and phosphoric acids on a mixture of sodium thiosulphate and formaldehyde in concentrated aqueous solution, whereas with concentrated hydrofluoric, hydrochloric, hydrobromic, and sulphuric acids, also 20% nitric acid, a deposit of thioform was produced. These results accord satisfactorily with the view that the intermediate hydroxymethylenethiosulphuric acid is produced in the case of the former set of acids, and that it undergoes decomposition, giving thioform in the presence of an excess of a very strong acid.

The separation of thioform from a solution of sodium thiosulphate, hydrochloric acid and formaldehyde is very slow, but if hydrogen sulphide is added, the formation of thioform occurs much more rapidly. It is therefore unlikely that the formation of thioform in the reaction under discussion arises from the interaction of formaldehyde with hydrogen sulphide produced by decomposition of thiosulphuric acid, and the probability of the intermediate occurrence of a hydroxymethylenethiosulphuric acid is confirmed. D. F. T.

Certain Cases of Abnormality with Grignard's Reaction. G. L. Stadnikov (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 887—889).—The interaction of ethyl formate and magnesium *iso*amyl bromide yields, not di*iso*amylcarbinol, but the corresponding formate, whilst that of ethyl formate and magnesium *iso*butyl bromide gives a mixture of di*iso*butylcarbinol and of the corresponding formate (compare Grignard, A., 1901, i, 250). The ethyl formate reacts comparatively slowly with the organo-magnesium compound, but the action yields a magnesium alkyl iodide corresponding with a secondary alcohol, and it would appear possible that the interaction of this with the ethyl formate gives rise to the above complex formates. Such an assumption is supported by the following experimental results.

In ethereal solution, magnesium benzhydryl iodide (1 mol.) and benzhydryl acetate (1 mol.) react neither in the cold nor at the boiling point of ether. Magnesium benzhydryl iodide (1 mol.) and ethyl acetate (2 mols.) yield, after decomposition of the product with water, benzhydryl acetate. Magnesium 2-methyl*cyclo*hexyl iodide and ethyl acetate yield 2-methyl*cyclo*hexyl acetate.

These experiments are to be extended with esters of organic and

inorganic acids; with the latter esters, magnesium alkyl iodides may react differently from alkyloxides of the type $(RO)_2Mg$ (compare Rabcevitsch-Zubkovski, A., 1912, i, 233). T. H. P.

Isomerisation of Higher Acids of the Series, $C_nH_{2n-2}O_2$, under the Influence of Potassium Hydroxide. I. V. Egorov (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 975—994). The fact that, when fused with alkali hydroxide, all unsaturated acids, independently of the position of their double linking, undergo rupture between the α- and β-carbon atoms indicates that decomposition of the acids is preceded by isomerisation. It has, indeed, been shown that, on prolonged boiling with aqueous or alcoholic alkali hydroxide, $\beta\gamma$-unsaturated acids are converted into the corresponding acids with an $\alpha\beta$-double linking, and that this change is reversible and takes place with formation of an intermediate β-hydroxy-acid. In the case of unsaturated acids in which the double linking is further removed from the carboxyl group than the $\beta\gamma$-position, such isomerisation under the influence of alkali hydroxide has not been observed. In order to obtain further information on this question, the author has studied the action of potassium hydroxide on oleic acid, with the double linking in the $\theta\iota$-position, and on undecenoic acid, with the double linking in the $\iota\kappa$-position.

When oleic acid is gently heated with potassium hydroxide solution, little, if any, isomerisation takes place, the principal compounds obtained by treatment of the product of the reaction with nitrogen peroxide and subsequent decomposition by means of hydrochloric acid in a sealed tube, being azelaic and pelargonic acids. If, however, the acid and alkali are heated together at 220—230°, the products obtained are: (1) palmitic acid; (2) *Δ^{δ}-octadecenoic acid*, $CH_3\cdot[CH_2]_{11}\cdot CH{:}CH\cdot[CH_2]_3\cdot CO_2H$, which crystallises in short needles, m. p. 42—43°, and, after combination with nitrogen peroxide and decomposition of the product by means of hydrochloric acid at 125—130°, yields glutaric and tridecoic acids; (3) the hydroxy-octadecoic acid, $CH_3\cdot[CH_2]_{11}\cdot CH(OH)\cdot[CH_2]_4\cdot CO_2H$ or $CH_3\cdot[CH_2]_{12}\cdot CH(OH)\cdot[CH_2]_3\cdot CO_2H$, which crystallises in lanceolate scales, m. p. 54—55°, and yields hydroxystearic acid when treated with acetic anhydride. Prolongation of the heating results in an increase in the proportion of palmitic acid formed and in a decrease in that of acid (2); the hydroxy-acid is always obtained in comparatively small yield.

In a similar manner, Δ^{ι}-undecenoic acid is converted by potassium hydroxide into *Δ^{θ}-undecenoic acid*, $CHMe{:}CH\cdot[CH_2]_7\cdot CO_2H$, b. p. 232°/190 mm., 274—276·5°/743 mm., D_0^0 0·9309, D_0^{25} 0·9119, which shows normal cryoscopic behaviour in acetic acid, but has double the normal molecular weight in freezing benzene. The following derivatives were prepared: *zinc* salt, m. p. 111—112°; *lead* salt, m. p. 78°; *copper* salt, m. p. 229—230°; *silver* salt; *ethyl* ester, b. p. 257—259°, 207—208°/185 mm., D_0^0 0·89655; *amide*, $C_{10}H_{19}\cdot CO\cdot NH_2$, m. p. 77—78·5°. Treatment of the ethyl ester, according to Bouveault's method, with sodium and absolute alcohol converts it into the *alcohol*, $C_{11}H_{22}O$, b. p. 244—245°/752 mm., D_0^0 0·8628,

D_4^0 0·86027, which yields the *phenylurethane*, $C_{18}H_{27}O_2N$, m. p. 46·5°. Decomposition of the acid by the nitrogen peroxide method yields principally acetic and azelaic acids, which are accompanied by suberic and, probably, propionic acids, the presence of a small proportion of the isomeric acid, $CHEt{:}CH\cdot[CH_2]_6\cdot CO_2H$, being thus indicated.

T. H. P.

Action of Phosphoric Oxide and of Zinc Chloride on Glycerides of Hydroxystearic and Ricinoleic Acids and the Accompanying Polymerisation. S. Fokin (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1027—1042).—By treating ricinoleic acid with hydrogen bromide and removing the elements of hydrogen bromide from the resultant dibromostearic acid by means of alcoholic potassium hydroxide, Chonovski (A., 1909, i, 760; *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1457) obtained two acids, to which he assigned the formulæ $CH_3\cdot[CH_2]_4\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$ and $CH_3\cdot[CH_2]_5\cdot CH{:}CH\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$. The investigations of Arnaud and Posternak (A., 1910, 356, 459) and of the author (A., 1914, i, 656) on the oleic acids from λ-hydroxystearic acid have, however, shown clearly that the removal of hydrogen bromide takes places in two different directions. Further, it has been shown that combination with hydrogen bromide occurs in two ways, that the removal of hydrogen bromide from the monobromostearic acid corresponding with Δ^{ι}-oleic acid gives three isomeric acids, $C_{18}H_{34}O_2$, with the double linking in the λ-, ι- and θ-positions respectively, and that λ-bromostearic acid, prepared from the hydroxystearic acid yielded by ricinoleic acid, gives Δ^{μ}- and Δ^{ν}-oleic acids. From these facts it appears that Chonovski was dealing with six isomeric acids. The results of Grün and Woldenberg (A., 1909, i, 284) are also criticised.

Further experiments now show that the polymerisation of the triglyceride of ricinoleic acid by treatment with zinc chloride leads, with intermediate formation of triglycerides of linoleic acid with conjugated double linkings, to compounds which exhibit the physical properties of caoutchouc and are polyprenes of a special type. China oil (compare A., 1913, i, 442) undergoes change in the same way as castor oil when treated with zinc chloride, but it appears probable that the linoleic (elæomargaric) acid present in this oil contains allenic double linkings.

T. H. P.

Separation of Dihydroxy- and Tetrahydroxy-stearic Acids. Hermann Matthes and Ludwig Rath (*Arch. Pharm.*, 1914, **252**, 699—703).—The mixture of unsaturated fatty acids obtained from *Strophanthus* oil is oxidised by alkaline potassium permanganate, the solution is decolorised and the manganese dioxide dissolved by sulphurous acid, and the precipitate is collected, washed with water, and dried in a vacuum over sulphuric acid. The unoxidised acids are extracted with light petroleum in a Soxhlet apparatus. The residual mixture is shaken with cold ether during twenty-four hours and is then extracted with ether in a Soxhlet apparatus. The ethereal solution and extract thus obtained contain dihydroxystearic acid, whilst the tetrahydroxystearic acid remains in the residue The separation is almost quantitative.

C. S.

Metallic Compounds containing Oxalo-complexes. II. Di-oxalo-compounds. A. WERNER [with W. J. BOWIS, A. HOBLIK, H. SCHWARZ, and H. SURBER] (*Annalen*, 1914, **406**, 261—331. Compare A., 1914, i, 803).—Two types of dioxalo-compounds have been examined. In substances of the first type, $[(NH_3)_3Co(C_2O_4)_2]R$ or $(NH_3)_3Co\begin{matrix}O\cdot CO\\ |\\ O\cdot CO\\ O\cdot CO\cdot CO_2R\end{matrix}$, one oxalo-group occupies two co-ordination positions, the other only one. In substances of the second type, $\left[A_2Cr\begin{matrix}(\cdot O\cdot CO\\ |\\ \cdot O\cdot CO)_2\end{matrix}\right]R$ (where A is NH_3, $\frac{1}{2}$en, or H_2O), each oxalo-group occupies two co-ordination positions.

I. *Dioxalotriamminecobalt salts*, $[(NH_3)_3Co(C_2O_4)_2]R$.—The free acid, which together with the sodium salt was obtained by Sörensen in 1899, has been prepared by boiling chloro-oxalotriamminecobalt with aqueous oxalic acid and also by evaporating to dryness a mixture of aqueous oxalic acid and oxalohydroxylotriamminecobalt. According to these methods of preparation the acid, which is a bluish-red, amorphous substance, belongs to the *cis*-series. Its salts, obtained by treating the acid with the requisite alkali, also show little tendency to crystallise; the *potassium* salt ($2H_2O$), *ammonium* salt ($2H_2O$), and *pyridine* salt, $[(NH_3)_3Co(C_2O_4)_2]H,C_5NH_5,2H_2O$, are described.

II. *Dioxalodiamminechromium salts*, $[NH_3)_2Cr(C_2O_4)_2]R$.—The *ammonium* salt, red needles containing $2H_2O$, is obtained, together with a by-product crystallising in dark violet needles, by the action of aqueous oxalic acid on dibromodiaquodiamminechromium bromide (an improved method of preparing this from Reinecke's salt is described) at 60° for a few minutes until the colour of the solution has changed to cherry-red or dark red. The following salts have been prepared by treating the ammonium salt with an aqueous solution of the metallic haloid; *potassium*, red needles containing $2H_2O$; *sodium*, stout, dark red, dichroic prisms; *lithium*, light red needles and leaflets; *rubidium*, light red needles, and *caesium*, dark red needles. The violet by-product appears to be $[(NH_3)_3Cr(C_2O_4)_2\cdot C_2O_4Cr(NH_3)_2(H_2O)_2]$, since it is converted into the preceding sodium salt by trituration with sodium iodide and a little water. These salts are very stable and can be crystallised from water.

III. *Dioxaloethylenediaminechromium salts*, $[en\ Cr(C_2O_4)_2]R$.—These salts are obtained from the additive *compound*,

$$[en\ Cr(C_2O_4)_2]K,KI,2H_2O,$$

bordeaux-red, monoclinic prisms, prepared by heating a mixture of red or blue potassium chromium oxalate and 10% ethylenediamine to the b. p., cooling, removing the precipitated by-product, and saturating the filtrate with solid potassium iodide. By treating the additive compound with aqueous silver nitrate at about 70° the *potassium* salt, $[en\ Cr(C_2O_4)_2]K$, dark red prisms containing $1H_2O$, is obtained; the *silver* salt, bordeaux-red, monoclinic prisms with $1H_2O$, *strontium*, small, red crystals with $2H_2O$, *aniline*, ruby-red needles, and *quinoline*, red needles, have been prepared. By treatment with concentrated

hydrobromic acid, these salts are converted into mono-oxalo-compounds, $[(H_2O)_2en\ Cr(C_2O_4)]Br$.

IV. *Dioxalodiaquochromium salts*, $[(H_2O)_2Cr(C_2O_4)_2]R$.—The isomeric relations of these substances and of their derivatives have been very fully investigated. Members of this class have been prepared by various investigators in 1842—1843 and by Werner (T., 1888, **53**, 404), and have been described as red chromium oxalates. The conflicting statements of these observers are due partly to incorrect estimations of the amount of water in the salts and partly to the failure to detect the occurrence of two series of salts. The red chromium oxalates of earlier investigators are shown to be *trans*-dioxalodiaquochromium salts; the new salts, which belong to the *cis*-series, are more violet in colour and are more readily soluble in water than the salts of the *trans*-series. Salts of the two series are easily distinguished by their behaviour with aqueous ammonia; *cis*-salts become green or yield a green solution, whilst *trans*-salts become brown or reddish-brown.

trans-Potassium dioxalodiaquochromium, $[(C_2O_4)_2Cr(OH_2)_2]K,3H_2O$, red crystals, and the sodium salt, rose-red, apparently rhombic leaflets containing $5H_2O$, are prepared by mixing hot, very concentrated aqueous solutions of oxalic acid and potassium or sodium dichromate. An anhydrous sodium salt, rose-red powder, is obtained (1) by moistening with water an intimate mixture of oxalic acid and sodium dichromate, (2) by double decomposition from the strontium salt and sodium iodide, and (3) by efflorescence of the hydrated salt. The following salts of the *trans*-series have also been prepared: by method (1), *lithium*, red mass; by method (2) from the sodium salt, *rubidium*, rose-coloured, crystalline powder containing $2\frac{1}{2}H_2O$, *caesium*, rose-coloured, crystalline meal, *ammonium*, red crystals containing $3H_2O$, *ethylenediamine*, rose-coloured, crystalline meal, *calcium* (from the potassium salt), rose-coloured, crystalline powder containing $16H_2O$, and *magnesium* (from the calcium salt), red, crystalline powder. The *strontium* salt, rose-coloured, crystalline meal containing $1H_2O$, and *barium* salt, pale red, crystalline powder containing $12H_2O$, are prepared by treating barium or strontium *trans*-dioxalohydroxyloaquochromium (see below) with hydrochloric acid. The trans-*lead*, *zinc*, and *silver* salts have also been prepared.

Salts of the cis*-series.*—*Potassium*, $[(C_2O_4)_2Cr(H_2O)_2]K,2H_2O$, lilac powder, is obtained by moistening a mixture of oxalic acid and potassium dichromate with water, and also by the prolonged heating of an aqueous solution of the *trans*-salt; *ammonium*, violet, crystalline powder containing $2H_2O$, is prepared from ammonium dichromate and oxalic acid in boiling aqueous solution; *rubidium*, violet, crystalline powder containing $\frac{1}{2}H_2O$, and *caesium*, dark violet, crystalline meal, are prepared from the aqueous solution of the ammonium salt and solid rubidium bromide or cæsium chloride.

V. *Dioxalohydroxyloaquochromium salts*, $\left[\begin{matrix}HO\\H_2O\end{matrix}Cr(C_2O_4)_2\right]R_2$.—These salts, both of the *cis*- and the *trans*-series, are obtained either by treating an aqueous solution of a salt of the dioxalodiaquochromium series with the corresponding metal hydroxide or by double decomposition.

The salts have an alkaline reaction and are reconverted into *cis*- or *trans*-dioxalodiaquochromium salts by dilute mineral acids. The salts of the *trans*-series are reddish-brown or brown, and are stable in the solid state; those of the *cis*-series are unstable and pale or dark green. The following have been prepared: *trans*-series, *potassium* ($1H_2O$), *sodium* ($4H_2O$), *lithium*, *rubidium* ($1H_2O$), *caesium*, *ammonium* ($2H_2O$), *ethylenediamine*, *calcium* ($6H_2O$), *strontium* ($6H_2O$), *barium* ($6H_2O$), *silver* ($1H_2O$), and *zinc*; *cis*-series, *potassium* ($2H_2O$), *rubidium*, *caesium*, *ammonium* ($1H_2O$), *barium* ($13H_2O$), *calcium*, and *silver* ($1H_2O$).

VI. *Dioxalodihydroxylochromium salts*, $[(C_2O_4)_2Cr(OH)_2]R_3$.—The *potassium* salt of the *trans*-series is obtained by treating potassium *trans*-dioxalohydroxyloaquochromium with concentrated aqueous potassium hydroxide. It is a pale blue substance containing $6H_2O$, is not very stable in the solid state, becomes green instantly in aqueous solution, and is converted into the *trans*-dioxalodiaquochromium salt by dilute acid. Similar properties are exhibited by the *silver* salt ($2H_2O$) and the *lead* salt. Salts of the *cis*-series are pale green, and are converted into *cis*-dioxalodiaquochromium salts by mineral acids; the *calcium* salt ($14H_2O$) and the *silver* salt ($4H_2O$) are described.

VII. *Dioxaloacetatoaquochromium salts*, $[(C_2O_4)_2Cr(OAc)(H_2O)]R_2$.—These salts are obtained by treating dioxalohydroxyloaquochromium salts with glacial acetic acid and a little water. They are stable only in the solid state, being decomposed even by cold water. Salts of the *cis*-series are blue or pale blue, those of the *trans*-series are rose-coloured. The following have been prepared: *trans*-series, *sodium*, *barium* ($7H_2O$), and *silver* ($3H_2O$); *cis*-series, *barium* ($7H_2O$), and *silver*.

VIII. *Dioxalodiacetatochromium salts*, $[(C_2O_4)_2Cr(OAc)_2]R_3$.—These salts, of the *cis*- and the *trans*-series, are similar in colour and behaviour to those of the preceding class. They are obtained by the action of glacial acetic acid and a little water on the dioxalodihydroxylochromium salts, or by treating the dioxalodiaquochromium salts with a large excess of an acetate. The following have been prepared: *trans*-series, *sodium* ($4H_2O$), and *silver* ($6H_2O$); *cis*-series, *silver* ($5H_2O$).

The unstable, green salts of the *cis*-dioxalohydroxyloaquochromium series (see above) are converted by loss of water into neutral salts, $\left[(C_2O_4)_2Cr\begin{smallmatrix}\cdot OH\cdot\\ \cdot OH\cdot\end{smallmatrix}Cr(C_2O_4)_2\right]R_4$, which can no longer be converted into *cis*-dioxalodiaquochromium salts by the action of dilute acids. The formation of these neutral salts is indicative of the juxta-position of the OH and the H_2O groups in the green dioxalohydroxyloaquochromium salts (and therefore also of the two H_2O groups in the violet dioxalodiaquochromium salts), and furnishes the main evidence for their *cis*-configuration. The brown dioxalohydroxyloaquochromium salts of the *trans*-series, like all other 1 : 6-hydroxyloaquo-salts, are characterised by great stability.

The following *tetraoxalodioldichromium salts* have been prepared: *ammonium*, $\left[(C_2O_4)_2Cr\begin{smallmatrix}\cdot OH\cdot\\ \cdot OH\cdot\end{smallmatrix}Cr(C_2O_4)_2\right](NH_4)_4,6H_2O$, dark green plates; *sodium*, lilac-red, dichroic crystals containing $4H_2O$.

Potassium *trans*-dioxalodiaquochromium (red potassium chromium

oxalate) reacts with glycine in boiling water to form *potassium dioxaloaminoacetatochromium*, $\left[(C_2O_4)_2Cr<\begin{matrix}NH_2\cdot CH_2\\ O---CO\end{matrix}\right]K_2,1\frac{1}{2}H_2O$, lilac, hygroscopic powder; the corresponding *barium* salt ($5H_2O$) has been prepared. By modifying the experimental conditions in the preparation of the preceding potassium salt, *potassium dioxalodiaminoacetatochromium*, $\left[(C_2O_4)_2Cr\left(\begin{matrix}NH_2\cdot CH_2\\ O---CO\end{matrix}\right)_2\right]K,H_2O$, bluish-red powder, has been prepared.

The green potassium cobaltic oxalate described by Durrant (T., 1905, **87**, 1781) has very probably the constitution

$$\left[(C_2O_4)_2Co\begin{matrix}OH\\ H_2O\end{matrix}\right]K_2,$$

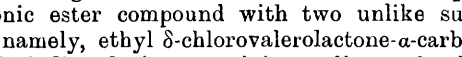
analogous to that of the dioxalohydroxyloaquochromium salt described above; it is converted into an almost black dioxalodihydroxylocobalt salt by treatment with an alkali. C. S.

Action of Magnesium on Esters of Bromosuccinic Acid. J. S. Zalkind (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 688—692).—Methyl or ethyl bromosuccinate reacts with magnesium in the same way as esters of monobasic acids; with the former ester, activation of the magnesium is necessary, but with the latter the presence of a crystal of iodine is sufficent. The products obtained, after decomposition by means of water, yield esters of: (1) fumaric acid, indicating loss of the elements of hydrogen bromide, similar to that occurring with ethyl α-bromo-α-phenylpropionate (compare Zalkind and Peschekerova, A, 1914, i, 959); (2) succinic acid; (3) both stereoisomerides of butane-αβγδ-tetracarboxylate, showing that the change proceeds partly in the direction of the Wurtz-Fittig reaction; (4) the pentabasic *hydroxy-acid*, $CO_2H\cdot CH_2\cdot CH_2\cdot C(OH)[CH(CO_2H)\cdot CH_2\cdot CO_2H]_2$, m. p. 257—259°, formed as a result of the condensation of three molecules of the bromomagnesium compound, $CO_2Et\cdot CH(MgBr)\cdot CH_2\cdot CO_2Et$; its *silver* salt, $C_{12}H_{11}O_{11}Ag_5$, was analysed; (5) apparently a very small proportion of succinylsuccinic acid, since a cherry-red coloration was obtained with ferric chloride.

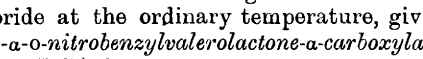
The formation of butanetetracarboxylic acid, and also the condensation of three molecules of the bromomagnesium ester, show that the reaction is of the type shown, not by the α-, but by the β-halogenated acids, the retarding action of the α-carboxyl group on the reactivity of the bromomagnesium group not being observed. If such retardation depends on the unsaturated character of the carboxyl, its absence in this instance may be explained by assuming that, in bromosuccinic esters, the two carboxyls saturate one another; the halogen is thus less firmly held and reacts in spite of the propinquity of the carboxyl group. T. H. P.

Spirans. V. Preparation of Mixed and Structurally Symmetrical Spirans in Stereoisomeric Forms. Hermann Leuchs and Herta Lemcke (*Ber.*, 1914, **47**, 2573—2585).—In the earlier publication (Leuchs and Radulescu, A., 1912, i, 179), a description has been given of the preparation of spirans by the formation of two

rings in a malonic acid derivative such as dibenzylmalonic acid; the resulting spirans were, however, produced from malonic acid or ester derivatives containing two like substituents. In the present investigation a malonic ester compound with two unlike substituents has been applied, namely, ethyl δ-chlorovalerolactone-α-carboxylate. This substance in alcoholic solution containing sodium ethoxide reacts with *o*-nitrobenzyl chloride at the ordinary temperature, giving after some days *ethyl δ-chloro-α-o-nitrobenzylvalerolactone-α-carboxylate*,

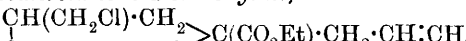


as an uncrystallisable oil which by reduction in aqueous alcoholic solution with zinc and hydrochloric acid is converted into *δ-chlorovalerolactone-dihydrocarbostyril-α-3-spiran*,

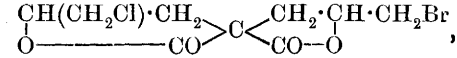


produced by intramolecular condensation of the primarily formed amino-compound. Both the parent nitro-compound and the spiran product contain two asymmetric carbon atoms, creating a possibility of four isomerides in each case; in the case of the former compound no separation was effected, although its oily nature may have been due to its lack of homogeneity; the spiran could be separated by fractional crystallisation from alcohol into two *isomerides*, hexagonal leaflets, m. p. 234—236°, and needles, m. p. 192—193°, respectively.

Interaction of *ethyl δ-chlorovalerolactone-α-carboxylate* with allyl bromide in alcoholic solution containing sodium ethoxide gave *ethyl δ-chloro-α-allylvalerolactone-α-carboxylate*,

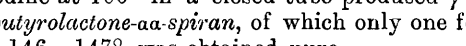


an oil, b. p. 186—188°/18 mm. Treatment with bromine in chloroform solution not only effected the addition of the element at the ethylenic linking, but also caused an elimination of ethyl bromide, the product being *γ-chloromethyl-γ'-bromomethylbisbutyrolactone-αα-spiran*,



from which three isomeric forms were isolated by crystallisation from alcohol, namely, lactone I, tetragonal and hexagonal tablets, m. p. 97—98°, lactone II, hexagonal leaflets, m. p. 133—134°, lactone III, needles or prisms, m. p. 145—146°. In an analogous manner the addition of iodine at 100° in a closed tube produced *γ-chloromethyl-γ'-iodomethylbisbutyrolactone-αα-spiran*, of which only one form, hexagonal leaflets, m. p. 146—147°, was obtained pure.

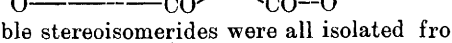
On treatment with a concentrated aqueous solution of hydrogen bromide, *ethyl δ-chloro-α-allylvalerolactone-α-carboxylate* was slowly converted into *γ-chloromethyl-γ'-methylbisbutyrolactone-αα-spiran*,



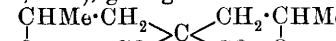
of the four possible isomerides only two, prisms, m. p. 68°, and needles, m. p. 83—84°, respectively, were obtained in a pure condition.

Unlike the preceding halogens and hydrobromic acid, chlorine

converts the parent ester into a symmetrical spiran compound, *bis*-γ-*chloromethylbutyrolactone-αα-spiran*,



The three possible stereoisomerides were all isolated from the product and were found, respectively, to consist of prisms, m. p. 98—99°, hexagonal leaflets, m. p. 114°, and hexagonal prisms, m. p. 134—135°.

The action of chlorine on a chloroform solution of ethyl diallylmalonate gives a mixture of three stereoisomeric forms of "dichlorononodilactone" (bis-γ-chloromethylbutyrolactone-αα-spiran), m. p. 99°, 144°, and 135° respectively. Hydrogen bromide in aqueous solution acts on diallylmalonic acid and its ester (as already described by Fittig and Hjelt, A., 1883, 456), giving nonodilactone (bis-γ-methylbutyrolactone-αα-spiran),  , the main product being that already described, m. p. 106°; but an *isomeride*, needles or leaflets, m. p. 110—111°, is now stated to be present to the extent of 1% of the reaction product.

The three supposedly stereoisomeric products of the interaction of bromine and ethyl diallylmalonate, namely, the three forms of dibromononodilactone, m. p. 158°, 110°, and 154·5° respectively, on reduction with aluminium and acetic acid at 100° give the same product, namely, diallylmalonic acid, thus confirming their structural identity.

D. F. T.

Conversion of Racemic Acid into a Mixture of Racemic and *d*-Tartaric Acids by means of *l*-Malic Acid. ALEX. MCKENZIE (T., 1915, **107**, 440—443).—Pasteur has stated that ammonium hydrogen *d*-tartrate combines with ammonium hydrogen *l*-malate to form a compound which when dissolved in aqueous ammonia has the same rotatory power as a mixture of equimolecular quantities of the two salts. In view of this statement, an attempt has now been made to resolve optically inactive acids by combining them with active acids.

On neutralising racemic acid (1 mol.) with aqueous potassium hydroxide and adding *l*-malic acid (1 mol.), a crystalline product separates which consists of a mixture of potassium hydrogen racemate and potassium hydrogen *d*-tartrate. The cause of this activation of racemic acid by malic acid cannot at present be satisfactorily explained.

Van't Hoff has suggested the possibility of rendering an inactive compound active by crystallising it from an optically active solvent. It has now been found that when potassium hydrogen racemate (1 mol.) is crystallised from an aqueous solution of *l*-malic acid (1 mol.), a mixture of potassium hydrogen racemate and potassium hydrogen *d*-tartrate is obtained. E. G.

Vanadyl Tartrates. G. A. BARBIERI (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 47—53).—The purple coloration observed when a vanadyl tartrate solution is made alkaline is due to the formation of a

complex salt. The following compounds were isolated and analysed: $(VO)C_4H_2O_6(NH_4)_2,2H_2O$, $(VO)C_4H_2O_6K_2,2H_2O$ and $(VO)C_4H_2O_6Na_2,3H_2O$.

They form violet crystals soluble in water. On electrolysis the coloured ion moves to the anode. The salts probably have the structure $VO<\begin{matrix}O\cdot CH\cdot CO_2R\\ O\cdot CH\cdot CO_2R\end{matrix}$. R. V. S.

Tetra-acetylmucyl Chloride and its Application to the Synthesis of Inositol. JOHANNES MÜLLER (*Ber.*, 1914, **47**, 2654—2656).—A claim for priority in the application of tetra-acetylmucyl chloride to the synthesis of inositol (compare Diels and Löflund, A., 1914, i, 1049).

Tetra-acetylmucyl chloride was prepared by the action of thionyl chloride on tetra-acetylmucic acid; hot alcohol converts the chloride into *diethyl tetra-acetylmucate*, m. p. 189°, and the action of ammonia on an ethereal solution of the chloride produces *tetra-acetylmucodiamide*, m. p. 290—292° (decomp.). D. F. T.

Derivatives of a New Form of Glucose. JAMES COLQUHOUN IRVINE, ALEXANDER WALTER FYFE, and THOMAS PERCIVAL HOGG (T., 1915, **107**, 524—541).—Fischer (this vol., i, 57) has given an account of the isolation of a third isomeric form of methylglucoside which he has termed γ-methylglucoside and which is very easily hydrolysed.

It is now shown that this γ-methylglucoside is a mixture of two isomeric hexosides derived from a new variety of glucose, and it has been found that, in addition to the properties recorded by Fischer, it is characterised by (1) the remarkable ease with which it condenses with acetone, (2) the readiness with which it reduces alkaline potassium permanganate solution, (3) its tendency to unite with one atomic proportion of oxygen to yield a neutral product, and (4) the ready auto-condensation of this oxy-compound to give a product allied to the disaccharides.

By repeated treatment with methyl iodide and silver oxide, γ-methylglucoside is converted into *tetramethyl γ-methylglucoside*, obtained as a colourless, mobile liquid, which is extremely easily hydrolysed by very dilute acids and instantly reduces cold alkaline permanganate; it has the following constants: b. p. 106°/0·25 mm., $[\alpha]_D$ in water −14·6°, $[\alpha]_D$ in alcohol −3·0°, n_D 1·4458, D_4^{15} 1·1064.

On hydrolysis with *N*/100-hydrochloric acid at 40°, tetramethyl γ-methylglucoside is converted into *tetramethyl γ-glucose*, a colourless, viscous liquid, which has b. p. 122°/0·05 mm., $[\alpha]_D$ in water −3·8° → −7·2°; $[\alpha]_D$ in benzene −17·1°, n_D 1·4585, and D_4^{15} 1·1644 (approx.). When tetramethyl γ-glucose was heated with phenylhydrazine and acetic acid, a dark-coloured compound was obtained which appeared to be of the nature of a hydrazone, but could not be purified. An anilide could not be prepared. By the action at 15° of methyl alcohol containing 0·25% of hydrogen chloride, tetramethyl γ-glucose is converted in a few minutes into the corresponding methylglucoside. On oxidation with alkaline permanganate, tetramethyl γ-glucose yields two products, one of which is a neutral liquid which does not reduce

Fehling's solution, and is possibly a tetramethylpentitol; the other compound, which constitutes the main product of the oxidation, is a new form of tetramethylgluconic acid, and on being heated in a vacuum is readily converted into a *tetramethylgluconolactone*, a syrupy liquid with $[\alpha]_D$ in alcohol $+59° \longrightarrow +46°$ in four hours, and n_D 1·4519. When tetramethyl γ-glucose is reduced with sodium amalgam, it yields a *tetramethyl sorbitol*, $OMe\cdot CH_2\cdot[CH(OMe)]_3\cdot CH(OH)\cdot CH_2\cdot OH$, b. p. 125/0·4 mm., n_D 1·4568 and $[\alpha]_D$ in water $-6·2°$; this specific rotation is permanent, but that of a solution of the compound in *N*/2-boric acid showed the following changes: after ten minutes, $-15·0°$: twenty-five minutes, $-8·2°$; thirty-five minutes, 0°; fifty minutes, $+6·8°$; 300 minutes, $-2·7°$ (constant). This optical exaltation indicates that the compound contains two hydroxyl groups attached to neighbouring carbon atoms (compare Böeseken, A., 1913, i, 1147).

When γ-methylglucoside is warmed with acetone, condensation takes place and γ-methylglucosidemonoacetone is probably formed. This compound was not isolated, but on treating the solution with methyl iodide and silver oxide two substances were obtained. One of these, *trimethyl oxy-γ-methylglucosidemonoacetone*, $C_{13}H_{24}O_7$, has b. p. 105—106°/0·025 mm., n_D 1·4493, and D_4^{15} 1·1133; on distilling this liquid, fractions of different rotatory power were obtained, indicating that it contained at least two isomeric compounds. The other substance, *anhydrobisdimethyl oxy-γ-methylglucosidemonoacetone*, $C_{24}H_{42}O_{13}$, is a viscous liquid, b. p. 200°/1·4 mm. and n_D 1·4587, and is probably a derivative, not of a hexose but of a disaccharide.

The constitution of γ-glucose and its derivatives is discussed, but it is shown that the data available are not sufficient to justify any definite conclusions. E. G.

Biochemical Synthesis of the β-Mono-*d*-galactoside of Ethylene Glycol. Em. Bourquelot, M. Bridel and A. Aubry (*Compt. rend.*, 1915, **160**, 571—573; *J. Pharm. Chim.*, 1915, [vii], **11**, 201—204).—Using the method already described for the preparation of the β-glucoside of ethylene glycol (compare A., 1913, i, 1080; 1914, i, 72) by means of emulsin, the authors have prepared *ethylene glycol β-mono-*d*-galactoside* in a crystalline form. It has m. p. 133—134°, is optically inactive, and is readily hydrolysed by dilute sulphuric acid or emulsin in aqueous solution. It has a slightly sweet taste and does not reduce Fehling's solution. W. G.

Chemistry of Starch. III. Hans Pringsheim and Franz Eissler (*Ber.*, 1914, **47**, 2565—2572. Compare A., 1913, i, 1156; 1912, i, 832; Schardinger, A., 1911, i, 181).—An extension to rice starch of the previous method of investigation by which crystalline dextrins have been obtained from potato starch.

When rice starch is fermented with *Bacillus macerans*, part of the starch separates, being unattacked by the organism. The solution on treatment with chloroform gives a deposit of crystalline dextrins from which dextrin-α (tetra-amylose), dextrin-β (β-hexa-amylose) and a "slime" can be separated, as was the case with potato starch (*loc. cit.*), but there is also present a new crystalline dextrin of which the

specific rotation, $[\alpha]_D^{20} + 123°$, is less than that of the dextrins known hitherto. The new dextrin is rather more soluble in water than is dextrin-β, but is only sparingly soluble in alcohol, from which it separates in microscopic needles. There are therefore now known six crystalline dextrins, four belonging to the α-group and two to the β-group. The former group comprises diamylose, $(C_6H_{10}O_5)_2$, tetra-amylose, $[(C_6H_{10}O_5)_2]_2$, the "slime" and the new dextrin; reasoning from the relative solubilities of these substances, the "slime" is believed to be an octasaccharide, $[(C_6H_{10}O_5)_2]_4$, and the new dextrin a trisaccharide, *α-hexa-amylose*, $[(C_6H_{10}O_5)_2]_3$, isomeric with dextrin-β, $[(C_6H_{10}O_5)_3]_2$. The conversion of a member of the α-group into the β-group as effected with tetra-amylose by heating with glycerol at 200° (A., 1913, i, 1156) is now shown to give triamylose as product.

α-Hexa-amylose, like its companions in the α-group, gives an additive compound (green needles) with iodine when treated with an aqueous solution of iodine in potassium iodide, and the crystalline dextrins as a class are found to yield similar crystalline additive compounds both with iodine and bromine. The iodine and bromine additive compounds of the crystalline dextrins of the β-group form deep brown and yellow prisms respectively, whereas those of the α-group form long needles, respectively dark green and yellow. The following additive compounds were prepared: *β-hexa-amylose tri-iodide*, $(C_6H_{10}O_5)_6,9H_2O,3I$; *triamylose iodide*, $(C_6H_{10}O_5)_3,4\frac{1}{2}H_2O,1\frac{1}{2}I$; *tetra-amylose iodide*, $(C_6H_{10}O_5)_4,4H_2O,1\frac{1}{2}I$; *diamylose iodide*, $(C_6H_{10}O_5)_2,\frac{3}{4}I$; *β-hexa-amylose dibromide*, $(C_6H_{10}O_5)_6,2Br$; *triamylose bromide*, $(C_6H_{10}O_5)_3,Br$; *octa-amylose tribromide*, $(C_6H_{10}O_5)_8,3Br$; *tetra-amylose bromide*, $(C_6H_{10}O_5)_4,1\frac{1}{2}Br$; *diamylose bromide*, $(C_6H_{10}O_5)_2$ with $\frac{3}{4}$ or 1 Br.

On account of their general freedom from combined water, the bromine additive compounds are of value for purposes of analysis.

D. F. T.

Cellulose Acetates. E. KNOEVENAGEL (*Zeitsch. angew. Chem.*, 1914, **27**, 505—509).—A brief review of earlier work is followed by an account of the author's own experiments in the production of acetone-soluble cellulose acetates. Acetylation of cellulose by means of acetic anhydride, using sulphuric acid as a catalyst, is accompanied by such extensive acetolysis that the product, although soluble in acetone, is lacking in viscosity and tensile strength, but the cellulose acetates, insoluble in acetone, produced without simultaneous acetolysis by the use of milder catalysts, such as the aromatic hydrogen sulphates, are converted into acetone-soluble products without appreciable hydrolysis of the acetyl groups by the action of heat with or without a catalyst. Thus soluble cellulose acetates were formed when the insoluble acetylation products were heated with ethyl acetate, benzene, acetone, alcohol, acetylene tetrachloride, etc., at temperatures above 100° in the absence of both water and catalysts. The conversion, however, was much accelerated by the presence of suitable catalysts, such as sodium ethyl sulphate, methylamine hydrogen sulphate with 10% of the normal salt, and *o*-toluidine hydrogen sulphate, and the exclusion of water in these circumstances was

also found to be undesirable. The acetylation of the cellulose was carried out at 70° with a mixture of acetic acid and anhydride to which 0·1 part of one of the above catalysts was added. The solution of cellulose hexa-acetate thus obtained was then directly converted into an acetone soluble product by destroying the excess of acetic anhydride by the addition of water, 0·8 part, and heating the resulting acetic acid solution at 54·7°. Determinations of the acetyl and copper values, and the solubility, from time to time showed that the former had only decreased at most 1% by the time an acetone-soluble product had been obtained (14—73 hours according to the catalyst employed), and that the copper number had actually decreased. Only on prosecuting the reaction far beyond this stage did subsidiary action, hydrolysis, etc., become evident by a decrease in the acetyl value and a rise in the copper number. Eventually gelatinisation set in. Further experiments on previously isolated cellulose acetates showed that the same transformation, although slower, occurs in 99% acetic acid without a catalyst, and that it is accelerated by the presence of small quantities of water and alcohol, and also by normal salts, such as methylamine sulphite, ammonium nitrate, etc. So also in aniline solution, in the absence of water, and with or without catalysts, the transformation to acetone-soluble cellulose acetates occurred, without either hydrolysis or acetolysis, as is asserted by Schering and Loose in various patent specifications. The production of acetone-soluble cellulose acetates merely by the action of heat, accelerated, if desired, by catalysts, is therefore not attributable to partial hydrolysis of acetyl groups or of the cellulose molecule itself. The author considers that the change is of the nature of an isomerisation within the cellulose acetate molecule, and belongs to the same category as that producing the multirotation phenomena in the sugar group.

The acetyl determinations required in the investigation were carried out by warming the dried substance with 75% alcohol at 50—60° for half an hour, adding to the swollen mass $N/2$-potassium hydroxide in excess, warming at 50°, and allowing to cool slowly for twenty-four hours with frequent shaking. The excess of hydroxide was then estimated by titration. G. F. M.

The System Nitroglycerin [Glyceryl Trinitrate]—Nitrated Cotton. I. Condensation of Vapours of Nitroglycerin on Nitrated Cotton in a Vacuum at Uniform Temperature. II. Extraction of Nitroglycerin from Ballistite by Distillation in a Vacuum at Ordinary Temperature. D. Chiaraviglio and O. M. Corbino (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 247—250, 361—366. Compare A., 1913, i, 1299).—When glyceryl trinitrate and nitrated cotton are placed in the same vessel, which is highly evacuated and is kept at 30°, the glyceryl trinitrate exhibits a diminution in vapour pressure and migrates to the nitrated cotton. When the latter is devoid of fibrous structure, as is the case with ballistite freed from glyceryl trinitrate by extraction with ether, a similar phenomenon is observed. The action appears to consist of an imbibition, similar to that occurring between cellulose and water. That the nitrated cotton is not merely dissolved in the glyceryl trinitrate is shown by a rise of

temperature, amounting to several degrees, which takes place when glyceryl trinitrate is allowed to fall on to nitrated cotton.

Even at the ordinary temperature, ballistite in a high vacuum loses glyceryl trinitrate at an appreciable rate, which increases markedly as the temperature is raised. This result also is analogous to that obtained under similar conditions with the system cellulose–water. The residue from the ballistite is unchanged in appearance, but of slightly increased rigidity. The loss of glyceryl trinitrate is accompanied by the evolution of gas which has not yet been examined.

T. H. P.

Molecular Compounds of Amines. A. KOTSCHUBEI (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1048—1055).—Amines combine with many different organic and inorganic compounds to form molecular compounds, and the salts obtained on partial oxidation of aromatic diamines must also be regarded as molecular compounds.

The action of potassium ferricyanide on *p*-phenylenediamine (compare Bandrowski, A., 1894, i, 236; Willstätter and Mayer, A., 1904, i, 511) in cold aqueous solution yields a dark blue, almost black compound having the properties of a meri-quinonoid salt. Hydroferrocyanic acid and *p*-phenylenediamine give an almost white meri-quinonoid compound, $4C_6H_8N_2,Fe(CN)_6,2H_2O$. *p*-Leucaniline and potassium ferricyanide in aqueous alcohol yield a dark blue compound,

$$[CH(NH_2Ph)_3]_4,Fe(CN)_6,3H_2O.$$

The molecular compounds of the amines form four classes, formed from: (1) Salts of amines and metallic salts, halogens or inorganic compounds, such as $(NH_2Me,HCl)_2,HgCl_2$, NMe_4I_9, etc.; (2) Amines and metallic salts, such as $(NH_2Me)_4,PbCl_4$, $3C_2H_4(NH_2)_2,ZnCl_2$, etc.; (3) Amines and inorganic compounds or halogens, such as NMe_3,CS_2, $C_4H_{10}N_2,6H_2O$, $C_6H_{12}N_4,I_4$, etc.; (4) Amines and organic compounds, such as $[CHPh(C_6H_4\cdot NH_2)_2],C_6H_6$, $NH_2Ph,C_6H_3(NO_3)_3$, etc. The structures of many of these compounds and also of those obtained by the author and described above are explainable according to Werner's theory.

T. H. P.

Hexamethylenetetramine Trichloroacetate. L. VANINO (*Arch. Pharm.*, 1914, **252**, 400).—Trichloroacetic acid, about 81·7 grams, is triturated with 5 c.c. of water, and the mixture is added to an aqueous solution, as concentrated as possible, of hexamethylenetetramine (70 grams in 115 c.c.); by keeping the solution in a freezing mixture, hexamethylenetetramine trichloroacetate, $C_6H_{12}N_4,CCl_3\cdot CO_2H$, is rapidly precipitated.

The anti-bacterial action of a solution (1 : 400) is about the same as that of a solution of formaldehyde (1 : 80,000), and completely prevents bacterial growth.

C. S.

Compounds of Hexamethylenetetramine. L. VANINO and A. SCHINNER (*Arch. Pharm.*, 1914, **252**, 449—459).—Contrary to statements in the literature, hexamethylenetetramine and salts of copper, cadmium, iron, cobalt, and nickel in aqueous solution readily yield additive compounds provided the solution is sufficiently concen-

trated. The brownish-yellow *cuprichloride*, $C_6H_{12}N_4,2CuCl_2$, green *cupriacetate*, $C_6H_{12}N_4,2Cu(OAc)_2$, *cobaltonitrate*, $2C_6H_{12}N_4,Co(NO_3)_2,9H_2O$, red, crystalline powder, *nickelonitrate*, $2C_6H_{12}N_4,Ni(NO_3)_2,9H_2O$, green powder, *cadmisulphate*, $C_6H_{12}N_4,CdSO_4,6H_2O$, colourless, prismatic crystals, *manganochloride*, $2C_6H_{12}N_4,MnCl_2,8H_2O$, colourless, prismatic crystals, *calcichloride*, $2C_6H_{12}N_4,CaCl_2,6H_2O$, colourless, crystalline powder, and *mercurocyanide*, $C_6H_{12}N_4,3Hg(CN)_2,1\frac{1}{2}H_2O$, colourless, hexagonal crystals, have been prepared.

Hexamethylenetetramine in dry benzene reacts with an excess of phthaloyl chloride to form a gelatinous precipitate; this is converted by drying into a colourless, horny substance, which appears to have the composition $C_6H_{12}N_4,C_6H_4<\begin{matrix}CCl_2\\CO\end{matrix}>O$. C. S.

Attempts to Convert Choline into Neurine. ERNST SCHMIDT (*Arch. Pharm.*, 1914, **252**, 708—711).—Unsuccessful attempts have been made to convert choline into neurine directly by means of sulphuric acid, phosphoric oxide, zinc chloride, and phosphoryl chloride, also by heating the platinichloride with concentrated sulphuric acid at 125—130°. The platinichloride alone, heated at its m. p., yields trimethylamine and ammonium platinichlorides. C. S.

Alkylated *iso*Acylglycine Ethers and Phenylhydrazonoethers. ERICH SCHMIDT (*Ber.*, 1914, **47**, 2545—2550).—In order to throw further light on the condensation of imino-ethers with hydroxylamine hydrochloride, producing oximinocarbonic esters (Houben and Schmidt, A., 1913, i, 958; 1914, i, 26), the author has submitted several imino-ethers to treatment with the hydrochlorides of various bases with the result that the imino-hydrogen is shown to be generally reactive.

For the preparation of imino-ethers it was found convenient to allow the nitrite, alcohol and hydrogen chloride to react under a layer of light petroleum in a special apparatus in a freezing mixture of ice and salt. Chloroacetonitrile was in this manner converted into *ethyl chloroacetimino-ether hydrochloride*, $CH_2Cl\cdot C(NH)\cdot OEt,HCl$.

Acetonitrile, ethyl mercaptan, and hydrogen chloride underwent quantitative condensation with formation of *ethyl thiolacetimino-ether hydrochloride*, $NH{:}CMe\cdot SEt,HCl$, prismatic crystals, which does not yield ammonium chloride when warmed in alcoholic solution.

When an ethereal solution of the imino-ether obtained from acetonitrile and ethyl alcohol was shaken with a cold aqueous solution of glycine ester hydrochloride, the *ethyl ether* of *ethyl* iso*acetylglycine*, $OEt\cdot CMe{:}N\cdot CH_2\cdot CO_2Et$, was obtained as a pleasant smelling oil, b. p. 58—59°/0·27 mm.; the *ethyl* ester of the corresponding *methyl*iso*acetylglycine*, $OMe\cdot CMe{:}N\cdot CH_2\cdot CO_2Et$, was an oil, b. p. 56—57°/0·33 mm. The analogous *ethyl* ester of *methyl*iso*propionylglycine*, $OMe\cdot C(CH_2Me){:}N\cdot CH_2\cdot CO_2Et$, had b. p. 59—60°/0·25 mm.

When acetiminoethyl ether in ethereal solution is shaken with a cold aqueous solution of phenylhydrazine hydrochloride, *acetophenylhydrazonoethyl ether*, $NHPh\cdot N{:}CMe\cdot OEt$, is obtained as an amber-

yellow, viscous oil, b. p. 145—147°/13 mm. The analogous and isomeric *propionophenylhydrazonomethyl ether*,

$$NHPh\cdot N{:}C(CH_2Me)\cdot OMe,$$

is a yellow liquid, b. p. 88—89°/0·29 mm., 148°/12 mm. (slight decomp.). D. F. T.

Action of Sodium Hypochlorite on Amides of α-Hydroxy-acids. A New Method for the Degradation of Sugars. R. A. WEERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1163—1167).—The method adopted for the degradation of amides of αβ-unsaturated acids (A., 1913, i, 1195) is also applicable to amides of α-hydroxy-acids.

Mandelamide was converted into benzaldehyde on treatment with sodium hypochlorite, and since benzylidene-azine, benzaldehydesemicarbazone and azodicarbonamide were produced when hydrazine sulphate was added to the reaction mixture, it was concluded that sodium *iso*cyanate was also a product of the main reaction, which proceeded therefore in a manner analogous to the Hofmann reaction:

$$C_6H_5\cdot CH(OH)\cdot CO\cdot NH_2 \longrightarrow C_6H_5\cdot CH(OH)\cdot CO\cdot NHCl \longrightarrow C_6H_5\cdot CH(OH)\cdot N{:}C{:}O \longrightarrow C_6H_5\cdot CHO + HN{:}C{:}O$$

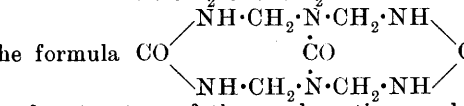
By applying the reaction to the amides of the hydroxy-acids of the sugar series, a degradation of the original sugar was achieved. d-*Gluconamide*, m. p. 142—143°, $[\alpha]_D^{12}$ + 33·8°, prepared by passing ammonia into an alcoholic solution of the crude gluconolactone, was thus converted into *d*-arabinose, which was isolated in 50% yield as its diphenylhydrazone, m. p. 202—203° (uncorr.). The sugar was liberated with formaldehyde, it had m. p. 156—157°, $[\alpha]_D^{10}$ − 105·7° (twenty-four hours after dissolving).

In a similar way *d*-galactose was converted through *d*-galactonamide into *d*-lyxose, isolated as its *p*-bromophenylhydrazone, m.p. 156—157°. G. F. M.

Hydrogen Peroxide. II. Tetramethylenedicarbamide Diperoxide. C. VON GIRSEWALD and H. SIEGENS (*Ber.*, 1914, **47**, 2464—2469).—It is already known that hexamethylenetetramine can form compounds with hydrogen peroxide (von Girsewald A., 1912, i, 835), and a compound of hydrogen peroxide with carbamide has already been introduced into commerce; since formaldehyde gives a condensation product with carbamide, the authors have been encouraged to attempt the synthesis of a peroxide compound from this condensation product and hydrogen peroxide.

When a solution of the condensation product of formaldehyde and carbamide in nitric acid is treated with hydrogen peroxide, or when a mixture of carbamide, 30% hydrogen peroxide and 35% formaldehyde solution is treated in the cold with nitric acid (D 1·4), *tetramethylenedicarbamide diperoxide* separates in needles, m. p. above 175° (decomp.). The new substance is sparingly soluble in most solvents, but dissolves in nitric and sulphuric acids; when boiled with dilute acids or alkalis it is quantitatively resolved into its constituents or their decomposition products; the substance explodes when heated directly by a flame. On account of the lack of a suitable solvent, the

molecular weight of this substance could not be determined, but the constitution $CO<^{NH\cdot CH_2\cdot O\cdot O\cdot CH_2\cdot NH}_{NH\cdot CH_2\cdot O\cdot O\cdot CH_2\cdot NH}>CO$ is attributed to it, whilst the formula



is believed to represent the structure of the condensation product of formaldehyde and carbamide.

Hydrazine, formaldehyde, and hydrogen peroxide have also been found to condense, giving an organic peroxidic *substance*, the investigation of which is still incomplete. D. F. T.

Platinum Compounds of *iso*Nitriles [Carbylamines] which contain a Cyano-radicle. L. Tschugaev and P. Teearu (*Ber.*, 1914, **47**, 2643—2647).—In a recent communication (Tschugaev and Teearu, A., 1914, i, 392) it has been shown that carbylamines form additive complexes with platinous chloride. The compounds generally were of the composition $[Pt(R\cdot NC)_4]PtCl_4$, and were resolved by heating into the monomeric substances, $[Pt(R\cdot NC)_2]Cl_2$, but the *tert.*-butyl compound, $[Pt(CMe_3\cdot NC)_4]PtCl_4$, was exceptional in failing to pass easily into the monomeride, and is now found to behave peculiarly towards excess of the carbylamine.

If the deep red compound, $[Pt(CMe_3\cdot NC)_4]PtCl_4$, is shaken with excess of *tert.*-butylcarbylamine, it dissolves to a colourless solution, containing an unstable *compound*, $[Pt(CMe_3\cdot NC)_4]Cl_2$, the solution of which can only be kept unaltered for a few hours even at 0°; at higher temperatures it gives a yellow, fluorescent jelly, which soon crystallises in needles; this new substance is a *platinum di*-tert.-*butylcarbylamine dicyanide*, $[Pt(CMe_3\cdot NC)_2](CN)_2$, which is resolved into the free carbylamine and potassium platinocyanide by potassium cyanide, and can be obtained synthetically from platinous cyanide and *tert.*-butylcarbylamine directly by the addition of water to a mixture in aqueous alcoholic solution. In this method of preparation, the mixing of the two reagents in aqueous alcoholic solution is accompanied by a partial separation as a red solid, which is isomeric with the above yellow substance, and so is designated *β-platinum di*-tert.-*butylcarbylamine dicyanide*. This is obtained in a pure condition more readily by dissolving the earlier α-modification in much water, heating at 100°, and treating with a mixture of alcohol and *tert.*-butylcarbylamine, or by the action of *tert.*-butylcarbylamine on an aqueous solution of a soluble metallic platinocyanide in the presence of acetic acid. The β-modification consists of microscopic, red needles with a lustre resembling that of magenta; when heated alone or with suitable liquids, such as chloroform and alcohol (in which it is almost insoluble), it passes into the soluble α-modification. It is probable that the β-modification is a dimeric form, $[Pt(CMe_3\cdot NC)_4]Pt(CN)_4$, because the unstable solution mentioned above as containing a compound, $[Pt(CMe_3\cdot NC)_4]Cl_2$, immediately reacts with potassium or barium platinochloride, giving the red β-compound.

Other carbylamines can be made to yield compounds of this new

type by allowing a bimolecular proportion of carbylamine to act on a solution of potassium platinochloride and potassium cyanide in the molecular proportions 1 : 2. Under these conditions, methylcarbylamine gives an orange-yellow precipitate which soon becomes colourless, the latter *substance* forming needles of the composition

$$[Pt(MeNC)_2](CN)_2.$$

This is remarkably stable, and can also be obtained by heating silver platinocyanide with excess of methyl iodide in a sealed tube at 120—130° for six hours.

In an analogous manner to the last substance, the closely similar ethylcarbylamine derivative, platinum diethylcarbylamine dicyanide, $[Pt(EtNC)_2(CN)_2]$, can be obtained. D. F. T.

Action of Alkali-Metal Hydroxides on Sodium Nitroprusside. José Giral Pereira (*Anal. Fis. Quim.*, 1915, **13**, 144—154).—In solution in methyl alcohol, sodium hydroxide reacts with sodium nitroprusside in accordance with the equation :

$$Na_2Fe(NO)(CN)_5,2H_2O + 2NaOH = Na_4Fe(NO_2)(CN)_5,H_2O + 2H_2O.$$

Potassium hydroxide yields the analogous salt,

$$K_2Na_2Fe(NO_2)(CN)_5,H_2O.$$

Ammonium hydroxide reacts differently, the product at 0° being the aminoprusside, $Na_3(NH_3)Fe(CN)_5$. The reaction at ordinary temperature corresponds with the equation : $Na_2Fe(NO)(CN)_5 + 3NH_3 + H_2O = Na_2(NH_4)Fe(CN)_5,NH_3 + NH_4NO_2$. A. J. W.

New Synthesis of Iminodiacetonitrile and its Conversion into Hydrazinodiacetic Acid. J. R. Bailey and D. F. Snyder (*J. Amer. Chem. Soc.*, 1915, **37**, 935—942).—As it appeared probable from the work of various authors that methyleneaminoacetonitrile, $CH_2{:}N{\cdot}CH_2{\cdot}CN$, would readily unite with hydrogen cyanide, experiments have been carried out which show that the reaction takes place at the ordinary temperature with formation of iminodiacetonitrile, $NH(CH_2{\cdot}CN)_2$. The hydrochloride of iminodiacetonitrile can be conveniently prepared by dissolving the nitrile in a 20% solution of hydrogen chloride in methyl alcohol; the *nitrate* has m. p. 134—135°. The *nitroso*-derivative, $NO{\cdot}N(CH_2{\cdot}CN)_2$, m. p. 38°, crystallises in pale yellow, slender prisms. The *benzoyl* derivative, $NBz(CH_2{\cdot}CN)_2$, m. p. 131—132°, forms diamond-shaped prisms. When a solution of iminodiacetonitrile in glacial acetic acid is treated with potassium cyanate and the product boiled with hydrochloric acid, and subsequently evaporated to dryness and boiled with 5% alcoholic solution of hydrogen chloride, ethyl hydantoin-1-acetate (Jongkees, A., 1908, i, 960) is produced.

Ethyl 2-thio-3-phenylhydantoin-1-acetate, $CO_2Et{\cdot}CH_2{\cdot}N\begin{matrix}CS{-}NPh\\ |\\ CH_2{\cdot}CO\end{matrix}$, m. p. 134°, crystallises in long, slender prisms; it was prepared by the following method. Iminodiacetonitrile was treated with *N*-sodium hydroxide and the solution boiled until ammonia ceased to be evolved. The solution was then neutralised with hydrochloric acid, evaporated to a small bulk, and boiled with an alcoholic solution of phenylthio-

carbimide. The solution was evaporated to dryness and the residue boiled with 5% alcoholic hydrogen chloride solution. *Ethyl 2-thio-3-methylhydantoin-1-acetate*, m. p. 62°, prepared in a similar manner by means of methylthiocarbimide, forms slender needles.

When methyl iminodiacetate hydrochloride is treated with sodium nitrite, methyl nitrosoiminodiacetate is produced, which on reduction with sodium amalgam is converted into hydrazinodiacetic acid.

E. G.

Nitroso-derivatives of Semicarbazinodiacetic Acid Esters. J. R. Bailey and D. F. Snyder (*J. Amer. Chem. Soc.*, 1915, **37**, 942—946).—Bailey and Read (A., 1914, i, 1055) have shown that methyl semicarbazinodiacetate reacts with nitrous acid with formation of methyl iminodiacetate. It is now shown that an intermediate nitroso-compound is produced in this reaction which, when left in the air, decomposes in a few hours with formation of methyl carbamidodiacetate.

Methyl nitrososemicarbazinodiacetate,

$$NH_2\cdot CO\cdot N(NO)\cdot N(CH_2\cdot CO_2Me)_2,$$

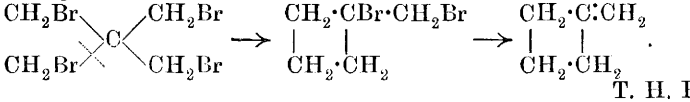
m. p. 67·5° (decomp.), crystallises in deep yellow, tetragonal prisms. The corresponding *ethyl nitroso*-ester, m. p. 60° (decomp.), separates from ether as a mass of hair-like needles.

Methyl carbamidodiacetate, $NH_2\cdot CO\cdot N(CH_2\cdot CO_2Me)_2$, m. p. 145° (decomp.), crystallises in prisms; it can also be prepared by the action of potassium cyanate on the hydrochloride of methyl iminodiacetate. When a solution of this compound in ethyl alcohol is treated with sodium ethoxide, it is converted into ethyl hydantoin-1-acetate, and similarly on treating a solution in methyl alcohol with sodium methoxide, methyl hydantoin-1-acetate is produced which has m. p. 114°, and not 107—108° as stated by Jongkees (A., 1908, i, 960).

Ethyl carbamidodiacetate, obtained by the decomposition of ethyl nitrososemicarbazinodiacetate or by the action of potassium cyanate on the hydrochloride of ethyl iminodiacetate, seems to exist in two forms, m. p. 76° and 80°. E. G.

Gustavson's So-called Vinyltrimethylene (Vinyl*cyclo*propane) and Ethylidenetrimethylene (Ethylidene*cyclo*propane). Al. Favorski and V. Batalin (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 726—729).—Demjanov found that the reduction of the crystalline nitrosite obtained by the action of nitrogen trioxide on Gustavson's "vinyltrimethylene" (A., 1896, i, 669) yields *cyclo*butanone (A., 1908, i, 329), and that the latter is also formed when this hydrocarbon is oxidised by means of permanganate. These results indicate that "vinyltrimethylene" is a derivative of *cyclo*butane and not of *cyclo*propane. Further, one and the same tertiary alcohol is obtainable from "vinyltrimethylene" and from "ethylidenetrimethylene," the latter hydrocarbon being prepared from the former by addition, and subsequent removal by the action of alcoholic potassium hydroxide, of hydrogen iodide (A., 1913, i, 451). The authors draw the conclusion that "vinyltrimethylene" and "ethylidenetrimethylene" are methylene-*cyclo*butane and 1-methyl-Δ^1-*cyclo*butene respectively, confirmation of this being furnished by the oxidation of the latter hydrocarbon to lævulic acid.

The mechanism of the formation of methylene*cyclo*butane is analogous to that of trimethylethylene from *tert.*-butyl bromide and may be represented thus:



T. H. P.

Chief Difficulties in the Treatment of the Orientation Question. Jul. Obermiller (*Zeitsch. angew. Chem.*, 1914, **27**, 483—485).—A theoretical paper. The main point is that it is apparently the influence exerted on ortho- and para-hydrogen atoms by orientating substituents which determines the position of the entering group. Ortho- and para-directing substituents increase the reactivity and facilitate the substitution of ortho- and para-hydrogen atoms; for example, phenol nitrates more readily than benzene, and gives *o*- and *p*-nitrophenols. Meta-directing substituents decrease the reactivity of ortho- and para-hydrogen atoms, and so the entering group takes the meta-position, but with diminished facility, as, for example, the further nitration of nitrobenzene. To this general conception there are numerous exceptions difficult of explanation. Thus, although replacement of hydrogen is hindered by the nitro-group, ortho- and para-chlorine atoms are given exceptional reactivity. Then the entering substituent and the conditions of reaction exert considerable influences, the nitro-group as such prefering to enter in the ortho-position, whilst the sulphonic group avoids this position. This is illustrated in cases where the meta-position is already occupied, as in *m*-toluic acid, which gives, mainly, the 2-nitro-acid, but the 4-sulphonic acid. Further difficulties are encountered in the fact that all substances containing ortho-para directing substituents are not substituted with greater facility than when these groups are lacking, as in the sulphonation of chlorobenzene.

G. F. M.

Interpretations of Some Stereochemical Problems in Terms of the Electronic Conception of Positive and Negative Valences. III. Continuation of the Interpretation of the Brown and Gibson Rule. IV. Simultaneous Formation of *o*-, *m*-, and *p*-Substituted Derivatives of Benzene. V. Reply to A. F. Holleman. Harry Shipley Fry (*J. Amer. Chem. Soc.*, 1915, **37**, 855—892).—In earlier papers (A., 1914, i, 263, 675) the author has employed the electronic conception of positive and negative valences and the electronic formula for benzene to explain the anomalous behaviour of many benzene derivatives and the mechanism of halogen substitution in the benzene nucleus and side-chain.

In the present papers, Brown and Gibson's rule is further considered and certain deductions are drawn. An explanation of the simultaneous formation of ortho-, meta-, and para-derivatives is advanced which is based on the conceptions of electronic isomerism and electronic tautomerism or the existence of electromerides in dynamic equilibrium; the mechanism of these changes is discussed. It is shown that the electronic formula for benzene and the electronic

rule for substitution are directly correlated with Holleman's hypotheses, and a reply is made to Holleman's objections to them (this vol., i, 9).

E. G.

The Bromination of *o*-Nitrotoluene. *o*-Nitrobenzylpyridinium Chloride. WILHELM GLUUD (*Ber.*, 1915, **48**, 432—435).—Hitherto the action of bromine on *o*-nitrotoluene has been understood not to be purely substitutive, but to be a more complex process, the isolated product being dibromoanthranilic acid (Greiff, A., 1880, 648). If, however, iron is used as a catalyst, the simple substitution of bromine into *o*-nitrotoluene can be easily effected, the product consisting mainly of 4-bromo-2-nitrotoluene. The product is very resistant to oxidation by potassium permanganate and only small quantities of 4-bromo-2-nitrobenzoic acid and a *substance*, m. p. 178°, possibly 6-bromo-2-nitrobenzoic acid, could be obtained. Oxidation by chromic acid in concentrated sulphuric acid solution gave a small quantity of bromonitrobenzaldehyde.

o-Nitrobenzylpyridinium chloride, prepared from *o*-nitrobenzyl chloride, is a colourless solid which separates with $1H_2O$ and then has m. p. 104—105°; when anhydrous, the m. p. is 203—204°. The yellow substance, m. p. 76°, obtained by Lellmann and Pekrun (A., 1891, 88), cannot have been pure.

D. F. T.

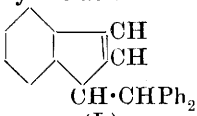
The Theory of the Oscillation of the Indene Double Linking. CH. COURTOT (*Compt. rend.*, 1915, **160**, 523—526).—The author has prepared certain 1- and 3-derivatives of indene and shown that there is no necessity for Thiele's theory of the oscillation of the double linking in the indene nucleus in the case of benzylindene (compare A., 1906, i, 569).

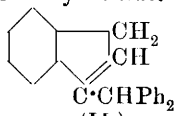
Acetone condenses with the magnesium derivative of indene to give 1-dimethylbenzofulvanol, b. p. 125°/8 mm. (compare A., 1911, i, 193; 1912, i, 250), which by means of alcoholic potassium hydroxide is converted into 3-dimethylbenzofulvanol, m. p. 82°. These two isomerides are distinguished by their behaviour on oxidation. With 5% aqueous potassium permanganate the former gives an *acid lactone*, m. p. 225°, which on boiling with barium hydroxide yields acetone and homophthalic acid, whilst the solid isomeride gives homophthalic acid directly.

Benzyl chloride reacts with the magnesium derivative of indene to give 1-*benzylindene*, b. p. 175—177°/14 mm., which with alcoholic potassium hydroxide gives 3-benzylindene, b. p. 185—187°/14 mm., m. p. 34° (compare Thiele, *loc. cit.*). These two isomerides are distinguished by their behaviour towards bromine. The 3-isomeride first fixes two atoms of bromine, which are eliminated almost immediately as hydrogen bromide, leaving phenylbenzofulvene. 1-Benzylindene gives a liquid *dibromide*, which does not spontaneously lose hydrogen bromide, and when treated with pyridine only yields resinous products.

The bromide of diphenylcarbinol condenses with the magnesium derivative of indene to give 1-*benzhydrylindene*, m. p. 161° (formula I). Diphenylbenzofulvene on hydrogenation yields 3-*benzhydrylindene*,

m. p. 115—116° (formula II), which can also be prepared from its 1-isomeride by the action of alcoholic potassium hydroxide.


(I.)


(II.)

W. G.

Interaction of Dibromomethyl Ether, $(CH_2Br)_2O$, and Benzene in Presence of Aluminium Bromide. I. L. Rabcevitsch-Zubkovski (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 698—704).—The principal product of this reaction is diphenylmethane, which is accompanied by considerable proportions of *m*- and *p*-dibenzylbenzenes and by traces of anthracene, toluene and resinous hydrocarbons of high boiling points; the yields of anthracene and toluene diminish as the excess of benzene taken is increased.

The first change is probably the interaction of aluminium bromide and dibromomethyl ether, with formation of dibromomethane, the subsequent stages being represented by the following equations (compare Friedel and Crafts, A., 1887, 1102): $CH_2Br_2 + 2C_6H_6 = CH_2Ph_2 + 2HBr$; $2CH_2Br_2 + 2C_6H_6 = C_6H_4\langle{}^{CH_2}_{CH_2}\rangle C_6H_4 + 4HBr$;

$C_6H_4\langle{}^{CH_2}_{CH_2}\rangle C_6H_4 + 2CH_2Br_2 = C_6H_4\langle{}^{CH}_{CH}\rangle C_6H_4 + 2HBr + 2MeBr$;

$MeBr + C_6H_6 = C_6H_5Me + HBr$. The isomeric dibenzylbenzenes are probably formed thus: $CH_2Br_2 + C_6H_6 = CH_2PhBr + HBr$ and $CH_2PhBr + CH_2Ph_2 = C_6H_4(CH_2Ph)_2 + HBr$. The formation of *m*- and *p*-dibenzylbenzenes, without the ortho-isomeride, is analogous to the results of Ador and Rilliet's experiments on the methylation of benzene (A., 1879, 228, 527). T. H. P.

Theory of Nitrating Mixtures in its Application to the Nitro-derivatives of Naphthalene. A. Saposhnikov (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1102—1110).—The author considers the results of Patart's investigation of the nitration of naphthalene (Mémorial des poudres et de salp., **9**, **11**) in the light of the theory of the action of nitrating mixtures developed by him in connexion with the nitration of cellulose (A., 1907, i, 390; A., 1910, i, 156). If the results are expressed in the form of a triangular diagram, it is found that here too the distribution of the different degrees of nitration in the diagram correspond moderately well with the vapour pressure curves of the nitric acid and consequently with the condition of the acid in the mixtures. For example, all the points corresponding with tetranitronaphthalene are found in that region of the acid mixtures where all the nitric acid exists in the form of free monohydrate, HNO_3. If the lines of the diagram representing equimolecular proportions of nitric and sulphuric acids are considered, it is seen that the degree to which the naphthalene is nitrated alters with the relative proportion of water present: with from 0 to 20—25% of water, tetranitronaphthalene is obtained; with 25—50%, trinitronaphthalene;

with 50—60%, di- and tri-nitronaphthalenes; with 60—65%, dinitronaphthalene, and with a still greater proportion, the mononitroderivative.

The similarity between the diagrams for the nitro-derivatives of naphthalene and cellulose no longer holds with acid mixtures approaching pure water or pure sulphuric acid. In general, nitration of cellulose is impossible when the acid contains more than 60—65 mol. % of water, whereas naphthalene may be nitrated by mixtures containing 75—80 mol. % of water. Increase of the sulphuric acid beyond a certain limit renders nitration impossible, since the excess of sulphuric acid decomposes the nitrated products; in the case of naphthalene, the latter is carbonised by an excessive proportion of sulphuric acid in the nitrating mixture. When naphthalene is nitrated to a high degree, the oxides of nitrogen liberated oxidise the nitro-products and diminish the yield. T. H. P.

The Condensation of Benzaldehyde and *iso*Amylamine. N. Ishizaka (*Ber.*, 1914, **47**, 2456—2460).—A special application of the reaction for the preparation of amines by heating an aldehyde or ketone with ammonium formate in the presence of a free acid (Wallach, Hüttner, and Altenburg, A., 1906, i, 160).

A mixture of *iso*amylamine and benzaldehyde with formic acid was maintained at boiling temperature for six to seven hours, when benzyl*iso*amylamine, $C_5H_{11}\cdot NH\cdot CH_2Ph$, and *dibenzyliso*amylamine, $C_5H_{11}\cdot N(CH_2Ph)_2$, b. p. 192—194°/19 mm., could be separated from the reaction product. The latter base (*hydrochloride*, m. p. 150—155°; *ferrocyanide*, crystalline scales) gave a *methiodide*, colourless needles, m. p. 154—155°; of which the corresponding quaternary ammonium *hydroxide* on decomposition by heat gave mainly dibenzyl*iso*amylamine with a smaller amount of *benzylmethyliso*amylamine, $C_5H_{11}\cdot NMe\cdot CH_2Ph$, b. p. 107—109°/12 mm., *hydrochloride*, m. p. 198—199°.

On carefully treating dibenzyl*iso*amylamine in the cold with a mixture of sulphuric and fuming nitric acids, there was obtained *dinitrodibenzyliso*amylamine, $C_5H_{11}\cdot N(CH_2\cdot C_6H_4\cdot NO_2)_2$ (*hydrochloride*, m. p. 186—187°), which by reduction with tin in a mixture of hydrochloric and acetic acids was converted into *diaminodibenzyliso*amylamine, $C_5H_{11}\cdot N(CH_2\cdot C_6H_4\cdot NH_2)_2$; *hydrochloride*, hygroscopic, amorphous powder; *platinichloride*, m. p. near 150° (decomp.); *acetyl* derivative. D. F. T.

The Preparation of Symmetrically Substituted Carbamides. Adolf Sonn (*Ber.*, 1914, **47**, 2437—2443).—The direct introduction of alkyl and aryl radicles into carbamide is especially conveniently effected by evaporating a mixture of carbamide and an amine with acetic acid; thus carbamide with a bimolecular proportion of a primary amine in the presence of acetic acid undergoes almost quantitative change, according to the equation: $2NH_2R + CO(NH_2)_2 = CO(NHR)_2 + 2NH_3$. Also, a monoalkylcarbamide on heating in acetic acid is converted into a symmetrical dialkylcarbamide as represented by $2NHPh\cdot CO\cdot NH_2 = CO(NHPh)_2 + CO(NH_2)_2$. In this type of chemical change, carbamide can be replaced by ammonium thiocyanate, which

gives an almost theoretical yield of *s*-diphenylcarbamide and hydrogen sulphide when heated for an hour with a bimolecular proportion of aniline in boiling acetic acid.

The new process proves exceptionally useful for the production of symmetrically substituted carbamides containing unlike alkyl groups, for the preparation of which the troublesome carbimides are generally necessary. A monoalkylcarbamide is allowed to react with a primary amine in the presence of acetic acid; in this way, ethylamine and *p*-ethoxyphenylcarbamide give rise to *p*-ethoxyphenylethylcarbamide, whilst phenylmethylcarbamide is obtained from methylcarbamide and aniline. For this type of change it is advisable to take only sufficient acetic acid for salt formation with the base as otherwise there is a danger of the formation of a diarylcarbamide. In the interaction of the carbamide with an aliphatic amine the process is not so simple as with an aromatic amine, and it is difficult to effect the formation of a dialkylcarbamide

In some cases it is found that the amine enters into reaction with the carbamide in equimolecular proportion only, examples of this behaviour being supplied by aminoazobenzene and β-aminoanthraquinone, which react with carbamide in acetic acid solution producing *benzeneazophenylcarbamide*, $NPh{:}N{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NH_2$, orange-red leaflets or prisms, m. p. 223—224° (*hydrochloride*, deep red), and *anthraquinonylcarbamide* respectively.

Very feebly basic amino-compounds such as glycine and anthranilic acid fail to give this reaction; *o*-nitroaniline is also recoverable unchanged from the mixture, but its *meta*-isomeride passes quantitatively into the corresponding *s*-carbamide.

Only primary amines are suited to this reaction, so that it is not possible to produce tetra-substituted carbamides in this manner; the failure of *s*-diphenylcarbamide to react with aniline under the described conditions is in accord with this result which recalls the similar shortcomings of the method for the preparation of alkylated carbamides from the corresponding alkylammonium carbamates (Fichter and Becker, A., 1912, i, 15). It is probable that the formation of a carbimide supplies an intermediate stage in the production of the substituted carbamide, in support of which view it is found that a certain quantity of *s*-diphenylmethylcarbamide is obtainable from methylaniline and phenylcarbamide, the latter substance being able to produce phenylcarbimide by elimination of water, whereas dialkylcarbamides do not react with primary amines.

No other solvent was discovered to give as good results as acetic acid, and it was not found possible to extend the method of substitution to thiocarbamide or guanidine. D. F. T.

Preparation of New Substituted Carbamides and Their Use for Stabilising Nitro-compounds. FABRIQUE PROD. CHIM. ORG. DE LAIRE, ISSY, FRANCE (*Eng. Pat.* 17501, July 23, 1914; from *J. Soc. Chem. Ind.*, 1915, **34**, 378).—Tetra-substituted carbamides, $NRR^1{\cdot}CO{\cdot}NR^2R^3$, where R and R^2 = aryl and R^1 and R^3 = alkyl, especially *α-phenyl-β-o-tolyl-α-methyl-β-ethylcarbamide*, *α-phenyl-β-o-tolyl-β-methyl-α-ethylcarbamide*, *αα-di-o-tolyl-β-methyl-β-ethylcarbamide*, and

αα-di-o-tolyl-ββ-diethylcarbamide, may be used for stabilising nitro-compounds, such as explosives or celluloid. They are viscous liquids or they melt below 50°, and are very soluble in organic media.

J. C. W.

Production of Carbamides of the Naphthalene Series. FARBENFABRIKEN VORM. F. BAYER & Co. (Fr. Pat. 471933, May 7, 1914; from *J. Soc. Chem. Ind.*, 1915, **34**, 347. Compare this vol., i, 14).—The process may be applied to other aminoacyl derivatives of 8-amino-α-naphtholsulphonic acid and of naphthylaminesulphonic acid.

J. C. W.

Thymol: Its Melting- and Solidifying-points. ROBERT MELDRUM (*Chem. News*, 1915, **111**, 193—195).—Recorded values for the m. p. of thymol vary from 44° to 50°. The author's freezing-point measurements give 48·2—49·2°. The higher value agrees fairly closely with the m. p. observations. Water lowers the m. p., and in presence of excess of water it was found to melt at 43°. H. M. D.

Preparation of Alkylaminoacylcatechols. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 277540; from *J. Soc. Chem. Ind.*, 1915, **34**, 303).—Arylsulphonyl haloids are allowed to act on salts of amino-acylcatechol ethers and alkali carbonates in an inert medium, such as acetone, water being added gradually as the reaction progresses. The arylsulphonylamino-derivatives thus obtained are then alkylated and finally saponified. J. C. W.

Formation of Dialkyloxyanilines in Reduction Processes. EUSTACE EBENEZER TURNER (T., 1915, **107**, 469—474).—In connexion with certain work on di-*o*-substituted benzenes, 2-aminoresorcinol diethyl ether was prepared. This compound has been described by Pukall (A., 1887, 662) as an easily oxidisable substance of m. p. 124°. As the product obtained by the author has m. p. 57° and was very stable, the present work was carried out which shows that Pukall's compound was not 2-aminoresorcinol diethyl ether, but probably consisted of 4 : 4′-diamino-3 : 5 : 3′ : 5′-tetraethoxydiphenyl.

2-Aminoresorcinol diethyl ether, $NH_2 \cdot C_6H_3(OEt)_2$, m. p. 57° (uncorr.), prepared by the reduction of 2-nitroresorcinol diethyl ether with tin and hydrochloric acid, crystallises in colourless needles; its *hydrochloride* and *platinichloride* were prepared. *2 : 6-Diethoxybenzeneazo-β-naphthol*, obtained by adding the diazotised amine to an alkaline solution of β-naphthol, forms deep red plates with a bright green reflex; it has m. p. 104° when heated slowly, but the m. p. varies with the rate of heating.

By the reduction of 2-nitroresorcinol dimethyl ether with tin and hydrochloric acid, Kauffmann and Franck (A., 1907, i, 1093) obtained 2-aminoresorcinol dimethyl ether; it has now been found that chloro-2-aminoresorcinol dimethyl ether is also produced in this reaction. *2-Aminoresorcinol dimethyl ether hydrochloride* and *platinichloride* have been prepared. *Chloro-2-aminoresorcinol dimethyl ether*, m. p. 50° (uncorr.), forms slender, colourless needles; its *hydrochloride* and *platinichloride* are described.

An attempt was made to convert 2-aminoresorcinol dimethyl ether into pyrogallol dimethyl ether by means of the method recommended by Cain (T., 1906, **89**, 19); a small quantity of a substance with the properties of pyrogallol dimethyl ether was produced, but it could not be obtained in a pure state. E. G.

Iron Compounds of Phenols. VII. Compounds of Eugenol and Vanillin with Iron. R. F. Weinland and Hermann Neff (*Arch. Pharm.*, 1914, **252**, 600—608. Compare Weinland and Binder, A., 1914, i, 553).—The following compounds of iron, containing the metal in the form of a complex anion, have been obtained by treating ferric acetate with an alkali hydroxide in absolute alcoholic solution; they are black, crystalline powders which appear violet or reddish-violet under the microscope, are insoluble in water, and are decomposed by acids or alkalis: *sodium tetravanillin-ferrate*, $[Fe\{O\cdot C_6H_3(OMe)\cdot CHO\}_4]Na,\frac{1}{2}H_2O$; *potassium pentavanillin-ferrate*, $[Fe\{O\cdot C_6H_3(OMe)\cdot CHO\}_5]K_2,H_2O$; *sodium tetraeugenol-ferrate*, $[Fe\{O\cdot C_6H_3(OMe)\cdot C_3H_5\}_4]Na,\frac{1}{2}H_2O$; *compound* of potassium tetraeugenol-ferrate and eugenol, $[Fe\{O\cdot C_6H_3(OMe)\cdot C_3H_5\}_4]K,C_3H_5\cdot C_6H_3(OMe)\cdot OH$. The last compound is always contaminated with the colourless potassium salt of eugenol, which is removed by washing with 96% alcohol. Eugenol and potassium hydroxide in absolute alcohol yield the *salt*, $C_3H_5\cdot C_6H_3(OMe)\cdot OK,2C_3H_5\cdot C_6H_3(OMe)\cdot OH$, colourless needles. C. S.

Studies in Phototropy and Thermotropy. VI. Polymorphic Vanillylidenearylamines Produced by Trituration and by the Influence of Actinic Light. Alfred Senier and Robert Benjamin Forster (T., 1915, **107**, 452—459).—Senier and Shepheard (T., 1909, **95**, 1951, 1954) have drawn attention to the phototropic and thermotropic properties exhibited by *p*-hydroxybenzylidene-*m*-toluidine and by vanillylidene-*m*-toluidine. Senier and Forster (T., 1914, **105**, 2462) have found that this polymorphic change is a general property of *p*-hydroxybenzylidenearylamines, and it is now shown that this is also true of the vanillylidenearylamines.

It has been observed that the deeper-coloured forms of the vanillylidenearylamines gradually revert to the paler varieties when they are removed from the influence of actinic light. Most of the bases exhibit thermotropy within certain limits of temperature. Phototropy was not detected among these bases or their polymorphic varieties, but, on exposure to sunlight for three or four months, most of them became much deeper in colour. The polymorphic varieties obtained by trituration generally show a deeper change of colour on prolonged exposure to actinic light than that exhibited by the original bases. Triboluminescence was not observed among these compounds. The following substances have been prepared and studied.

Vanillylideneaniline has m. p. 157° (corr.). Vanillylidene-*o*-, -*m*- and

-*p*-toluidines have m. p. 113—114° (corr.), 84° (corr.), and 119—120° (corr.) respectively. *Vanillylidene*-o-4-*xylidine*, $OH\cdot C_6H_3(OMe)\cdot CH{:}N\cdot C_6H_3Me_2$, m. p. 112—113° (corr.), forms pale yellow needles; *vanillylidene*-m-4-*xylidine*, m. p. 109° (corr.), forms colourless plates which rapidly turn brownish-yellow in sunlight; *vanillylidene*-p-*xylidine*, m. p. 103° (corr.), crystallises in pale yellow needles. *Vanillylidene*-ψ-*cumidine*, $OH\cdot C_6H_3(OMe)\cdot CH{:}N\cdot C_6H_2Me_3$, m. p. 123—124° (corr.), forms pale yellow needles. *Vanillylidene*-p-*chloroaniline*, $OH\cdot C_6H_3(OMe)\cdot CH{:}N\cdot C_6H_4Cl$, m. p. 128—129° (corr.), crystallises in nearly colourless prisms. *Vanillylidene*-m- and -p-*bromoanilines* have m. p. 70° (corr.) and 123—124° (corr.) respectively. *Vanillylidene*-p-*aminophenol*, $OH\cdot C_6H_3(OMe)\cdot CH{:}N\cdot C_6H_4\cdot OH$, begins to decompose at about 170° and melts at 201—202° (corr.). *Vanillylidene*-m- and -p-*anisidines*, $OH\cdot C_6H_3(OMe)\cdot CH{:}N\cdot C_6H_4\cdot OMe$, have m. p. 118—119° (corr.) and 132° (corr.) respectively. Vanillylidene-*o*-aminobenzoic acid has m. p. 169° (corr.). *Vanillylidene*-m-*aminobenzoic acid* is very sensitive to polymorphic change, and different specimens of equal purity have different m. p.'s. Vanillylidene-*p*-aminobenzoic acid forms yellow needles, which begin to decompose at about 200°, and melt at 213—214° (corr.). *Vanillylidenebenzidine*, $OH\cdot C_6H_3(OMe)\cdot CH{:}N\cdot C_6H_4\cdot C_6H_4\cdot NH_2$, begins to decompose at about 150° and melts at 184—186° (corr.). *Vanillylidene*-α- and -β-*naphthylamines*, $OH\cdot C_6H_3(OMe)\cdot CH{:}N\cdot C_{10}H_7$, have m. p. 113—114° (corr.) and 148—149° (corr.) respectively. E. G.

Aryl Chlorothiols. II. Th. Zincke (*Annalen*, 1913, **400**, 1—27. Compare A., 1912, i, 762).—Aryl hydroxythiols, Ar·S·OH, of the benzene series have not been obtained; an analogue in the anthracene series (anthraquinone-α-sulphenic acid) has been prepared by Fries (A., 1912, i, 1005).

[With S. Lenhardt.]—The product, m. p. 170°, obtained by boiling *p*-chloronitrobenzene with alcoholic sodium disulphide (Wohlfart, A., 1903, i, 203), is not a second modification of *pp'*-dinitrodiphenyl disulphide, as suggested by Blanksma in 1901, but is a mixture of the dinitrodiphenyl disulphide (m. p. 181°) and certain impurities. The pure disulphide is obtained by reducing an alcoholic solution of the product, m. p. 170°, with aqueous sodium sulphide and hydroxide, and oxidising the resulting mercaptan with ferric chloride; the alkaline mother-liquor contains *p*-nitro-*p'*-aminodiphenyl sulphide and the 4:4'-dinitrodiphenyl ether of *p*-azophenyl mercaptan (Fromm and Wittmann, A., 1908, i, 631).

p-*Nitrochlorothiolbenzene*, $NO_2\cdot C_6H_4\cdot SCl$, yellow crystals, m. p. 52°, is prepared like the *o*-isomeride (*loc. cit.*), and resembles it in its behaviour, except that it is less stable and yields sulphides directly by treatment with α- and β-naphthylamines. It is converted into *p*-nitrobenzenesulphonyl chloride, *p*-nitrobenzenesulphonic acid, and *pp'*-dinitrodiphenyldisulphoxide by nitric acid (D 1·4) in hot glacial acetic acid, into *p*-nitrophenyl thiocyanate by potassium cyanide in the same solvent, and by the action of water or, better, methyl or ethyl alcohol into p-*nitrothiophenyl oxide*, $O(S\cdot C_6H_4\cdot NO_2)_2$, yellow leaflets, m. p. 160°

(decomp.), blackening at 126°. The oxide is reconverted into the chlorothiol by phosphorus pentachloride, yields *pp'*-dinitrodiphenyl disulphide and the disulphoxide by continued treatment with methyl or ethyl alcohol or with acetic acid, and forms with alcoholic alkalis cherry-red solutions which doubtless contain the alkali salts of the hydroxythiol. These solutions yield *p*-nitrobenzenesulphinates and the disulphide by keeping, and the latter and the disulphoxide by acidification.

p-*Nitromethoxythiolbenzene*, $NO_2 \cdot C_6H_4 \cdot S \cdot OMe$, pale yellow needles, m. p. 49°, is prepared from dry sodium methoxide and the chlorothiol in benzene; it decomposes in moist air, yielding the disulphide, the disulphoxide, and the oxide. The isomeric p-*nitrophenylmethylsulphoxide*, $NO_2 \cdot C_6H_4 \cdot S \cdot OMe$, prepared by oxidising *p*-nitrophenyl methyl sulphide with nitric acid, forms colourless needles or leaflets, m. p. 149°.

p-Nitrobenzenesulphinic acid has m. p. 159°, sintering at 136°, and then darkening (Fromm and Wittmann, *loc. cit.*, gave 120°); its methyl ester, m. p. 141°, is identical with the sulphone obtained by oxidising *p*-nitrophenyl methyl sulphide with hydrogen peroxide in glacial acetic acid.

In general, *p*-nitrochlorothiolbenzene resembles the *o*-compound (*loc. cit.*) in its behaviour with ammonia and with amines. p-*Nitroaminothiolbenzene*, $NO_2 \cdot C_6H_4 \cdot S \cdot NH_2$, yellow needles, m. p. 103°, does not form salts with acids, but yields the *imine*, $NH(S \cdot C_6H_4 \cdot NO_2)$, pale yellow needles, m. p. 155°, and forms a *benzylidene* derivative, needles, m. p. 130°. p-*Nitromethylaminothiolbenzene*, $NO_2 \cdot C_6H_4 \cdot S \cdot NHMe$, yellow crystals, m. p. 48° (*methylimine*, $C_{13}H_{11}O_4N_3S_2$, faintly yellow needles, m. p. 156°), and the corresponding *dimethylaminothiol*, yellow crystals, m. p. 48°, *anilinothiol*, pale yellow leaflets or needles, m. p. 75°, and p-*toluidinothiol*, yellow needles, m. p. 73°, have been prepared.

4 p-*Nitrophenylthiol-α-naphthylamine*, $NO_2 \cdot C_6H_4 \cdot S \cdot C_{10}H_6 \cdot NH_2$, ochreous yellow needles, m. p. 168°, obtained approximately pure from the chlorothiol and α-naphthylamine in cold ether, forms a *hydrochloride*, colourless needles, and reacts again with the chlorothiol in chloroform to form 2 : 4-*di*-p-*nitrophenylthiol-α-naphthylamine*,

$$NH_2 \cdot C_{10}H_5(S \cdot C_6H_4 \cdot NO_2)_2,$$

golden needles, m. p. 171°, which can be diazotised and condensed with β-naphthol, and forms an unstable *hydrochloride* and a *diacetyl* derivative, $C_{26}H_{19}O_6N_3S_2$, pale yellow crystals, m. p. 181°.

A compound similar to the preceding is obtained from β-naphthylamine. 1-p-*Nitrophenylthiol-β-naphthylamine*, brown needles, m. p. 157°, forms a *hydrochloride*, colourless needles, and a *diacetyl* derivative, colourless leaflets, m. p. 160°, and reacts with the chlorothiol in chloroform to form 4-*nitro*-1(α-4'-*nitrophenylthiol-β-naphthylaminothiol*)-*benzene*, $NO_2 \cdot C_6H_4 \cdot S \cdot NH \cdot C_{10}H_6 \cdot S \cdot C_6H_4 \cdot NO_2$, yellow crystals, m. p. 195°. *p*-Nitrochlorothiolbenzene reacts with dimethylaniline in chloroform, yielding p-*nitro*-p'-*dimethylaminodiphenyl sulphide*,

$$NO_2 \cdot C_6H_4 \cdot S \cdot C_6H_4 \cdot NMe_2,$$

reddish-yellow leaflets, m. p. 156—157° (*hydrochloride*, pale yellow needles), and with the requisite phenol in ether to form p-*nitro*-p-*hydroxydiphenyl sulphide*, $NO_2 \cdot C_6H_4 \cdot S \cdot C_6H_4 \cdot OH$, stout, yellow needles,

m. p. 153—154° (*sodium* salt, deep red needles; *acetyl* derivative, faintly yellow needles, m. p. 80°), p-*nitrophenyl* 1-*hydroxynaphthyl sulphide*, yellow, crystalline powder, m. p. 172° (*acetyl* derivative, faintly yellow needles, m. p. 85°), p-*nitrophenyl* 2-*hydroxynaphthyl sulphide*, pale yellow needles, m. p. 176° (*acetyl* derivative, faintly yellow needles, m. p. 111°), and 4-*nitro*-2′ : 4′-*dihydroxydiphenyl sulphide*, yellow plates, m. p. 182° (*diacetyl* derivative, colourless leaflets, m. p. 115°).

The chlorothiol reacts with acetone to form p-*nitrophenyl acetonyl sulphide*, $NO_2 \cdot C_6H_4 \cdot S \cdot CH_2 \cdot COMe$, pale yellow leaflets, m. p. 71°, which dissolves in concentrated sulphuric acid with an orange-yellow colour and is precipitated unchanged by water. C. S.

Benzofulvanol and Benzofulvene. V. GRIGNARD and CH. COURTOT (*Compt. rend.*, 1915, **160**, 500—504. Compare Thiele, A., 1900, i, 298; 1906, i, 569; Manchot and Krische, A., 1905, i, 142).—*α-Benzofulvanol* (annexed formula) is obtained by heating dry trioxymethylene with the bromomagnesium derivative of indene in dry ether (compare A., 1911, i, 193; 1912, i, 250; 1914, i, 945) for five hours under reflux, while stirring constantly, and pouring the product on to ice mixed with ammonium chloride and ammonia to dissolve the magnesium hydroxide. The ethereal solution is then washed and dried, and the ether distilled off, leaving the required alcohol as a colourless, viscous liquid, b. p. 134°/10 mm., having an odour of roses. It unites with two atoms of bromine in chloroform solution and is very unstable on keeping, becoming more and more viscous and yellow in colour owing to dehydration and polymerisation. Attempts to dehydrate the alcohol with the usual agents were unsatisfactory, but by the application of Senderens' catalytic method, distilling it under reduced pressure in an atmosphere of carbon dioxide over alumina at 250°, *α-benzofulvene* (annexed formula) was obtained as a yellow liquid, crystallising immediately, giving greenish-yellow spangles, m. p. 37°, having a naphthalene-like odour. It rapidly fixes bromine and absorbs oxygen, and on keeping, even in a sealed tube, rapidly polymerises to a hard, yellow, vitreous mass, which, on heating, slowly deepens in colour to a reddish-brown and gives a pasty mass at 180°. Kept in a vacuum over sulphuric acid, benzofulvene partly sublimes and colours the acid red, but mainly polymerises. W. G.

Constitution of the β-Amino-αaβ-triphenylethyl Alcohol obtained by the Action of Light. LYDIA MONTI (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 143—146).—The author has investigated the compound, $C_{20}H_{19}ON$, obtained by Paternò by the interaction of benzophenone and benzylamine under the influence of light (A., 1914, ii, 321). When treated with nitrous acid, this base yields principally the dehydration product of triphenylethylene glycol obtained by Paternò and Forli-Forti (A., 1911, i, 66) and others. This product

is either triphenylethylene oxide or triphenylvinyl alcohol or can exist tautomerically in either form; its formation is explainable only on the assumption that the original compound, $C_{20}H_{19}ON$, is β-amino-$\alpha\alpha\beta$-triphenylethyl alcohol. T. H. P.

Hydrolysis of Esters by Activated Magnesium and the Etherate of Magnesium Iodide. J. ZALKIND (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 692—697).—The action of either magnesium and a small proportion of iodine or activated magnesium on esters of halogenated carboxylic acids sometimes gives rise to the products of hydrolysis of the esters. Thus, when methyl *p*-bromobenzoate, dry ether, magnesium and iodine are heated together in a sealed tube at 100°, the products obtained contain *p*-bromobenzoic acid. Methyl *m*-bromobenzoate also undergoes hydrolysis under these conditions, but to a less extent.

The course of this reaction and the effect on it of various conditions were investigated in the case of ethyl benzoate. When heated with magnesium alone, this ester remains unchanged; the presence of ether is not necessary and has little influence. The yield of the acid is increased by raising the temperature and, up to a certain limit, by prolongation of the heating. Under no conditions could complete hydrolysis be attained, owing partly to the establishment of a condition of equilibrium and partly to the fact that the reacting mixture becomes viscous and thus delays further action. It is found, indeed, that, although considerable diminution in the amount of magnesium iodide etherate taken lowers the yield of acid, slight diminution does not invariably do so.

The conclusion is drawn that this reaction proceeds according to the equations: $Ph\cdot CO_2Et + MgI_2 = Ph\cdot CO_2\cdot MgI + EtI$, and possibly, $Ph\cdot CO_2Et + Ph\cdot CO_2\cdot MgI = (Ph\cdot CO_2)_2Mg + EtI$. In presence of excess of magnesium, the ethyl iodide forms magnesium ethyl iodide, which (1) may react with the carboxyl group, giving the tarry products observed, and (2) may give rise to the butane which escapes when the tube is opened: $EtI + MgEtI = C_4H_{10} + MgI_2$. The magnesium iodide thus formed may then react with a further molecule of ethyl benzoate. T. H. P.

Preparation of Acetylsalicoyl [*o*-Acetoxybenzoyl] Chloride. R. WOLFFENSTEIN (D.R.-P. 277659; from *J. Soc. Chem. Ind.*, 1915, **34**, 303).—The acid is boiled with thionyl chloride in an inert solvent (benzene). J. C. W.

Organic Flavouring Materials. GEORG COHN (*Pharm. Zentr.-h.*, 1914, **55**, 735—747, 763—767).—The tastes of numerous representatives of three classes of compounds are described. In general, oximinoacetic acids form very sweet salts: *o*-aroylbenzoic acids are "bitter-sweet," and the tasteless or bitter benzotriazines form sweet sulphonic acids.

The following compounds appear to be new: p-*Tolylaldoximinoacetic acid*, $C_6H_4Me\cdot CH{:}N\cdot O\cdot CH_2\cdot CO_2H$, from the potassium salt of the

oxime and potassium chloroacetate, forms leaflets, m. p. 124°; o-*anisaldoximinoacetic acid*, m. p. 99—100°; p-*anisaldoximinoacetic acid*,

$$OMe\cdot C_6H_4\cdot CH{:}N\cdot O\cdot CH_2\cdot CO_2H,$$

broad needles, m. p. 111—114°; *piperonaldoximinoacetic acid*,

$$CH_2{:}O_2{:}C_6H_3\cdot CH{:}N\cdot O\cdot CH_2\cdot CO_2H,$$

glistening leaflets, m. p. 145°; o-*nitrobenzaldoximinoacetic acid*, yellow leaflets, m. p. 115°; p-*nitrobenzaldoximinoacetic acid*, m. p. 142°; *acetophenoneoximinoacetic acid*, $CPhMe{:}N\cdot O\cdot CH_2\cdot CO_2H$, m. p. 97—99°; *acetothienoneoximinoacetic acid*, $C_4SH_3\cdot CMe{:}N\cdot O\cdot CH_2\cdot CO_2H$; p-*methoxyacetophenoneoximinoacetic acid*, $OMe\cdot C_6H_4\cdot CMe{:}N\cdot O\cdot CH_2\cdot CO_2H$, m. p. 100—102°; *benzophenoneoximinoacetic acid*, $CPh_2{:}N\cdot O\cdot CH_2\cdot CO_2H$, m. p. 149—151°.

o-*Ethyltoluoylbenzoic acid*, from phthalic anhydride and *p*-ethyltoluene; o-*ψ-butylxyloylbenzoic acid*, $CMe_3\cdot C_6H_2Me_2\cdot CO\cdot C_6H_4\cdot CO_2H$; o-*styrenoylbenzoic acid*; o-2 : 4-*dihydroxytoluoylbenzoic acid*,

$$C_6H_2Me(OH)_2\cdot CO\cdot C_6H_4\cdot CO_2H,$$

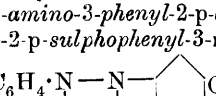
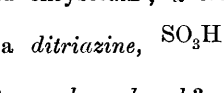
from orcinphthalein and sodium hydroxide; o-*methoxytoluoylbenzoic acid*, $OMe\cdot C_6H_3Me\cdot CO\cdot C_6H_4\cdot CO_2H$; o-*ethoxytoluoylbenzoic acid*; o-p'-*phenoxybenzoylbenzoic acid*, $OPh\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot CO_2H$; o-α-*methoxynaphthoylbenzoic acid*, $OMe\cdot C_{10}H_6\cdot CO\cdot C_6H_4\cdot CO_2H$, from α-naphthyl methyl ether, phthalic anhydride and aluminium chloride, m. p. 193°; o-β-*methoxynaphthoylbenzoic acid*; o-2'-*nitro*-4'-*dimethylaminobenzoylbenzoic acid*; o-4'-*methylethylaminobenzoylbenzoic acid*,

$$NMeEt\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot CO_2H,$$

m. p. 175—177°; o-4'-*diisoamylaminobenzoylbenzoic acid*; o-4'-*dimethylamino*-2'-*methylbenzoylbenzoic acid*, $NMe_2\cdot C_6H_3Me\cdot CO\cdot C_6H_4\cdot CO_2H$, m. p. 110°; the *nitro*-derivative of the last-named, m. p. 223° (decomp.); *diphenylpiperazinophthaloylic acid*, from diphenylpiperazine, m. p. 257° (decomp.); *kairolinphthaloylic acid*,

$$CH_2\!<\!\begin{matrix}CH_2\cdot CH_2\\ -NMe-\end{matrix}\!>\!C_6H_3\cdot CO\cdot C_6H_4\cdot CO_2H,$$

m. p. 199—203°, *hydrochloride*, m. p. 173—176°.

6-*Amino*-7-*hydroxy*-3-*phenyl*-2-p-*sulphophenyldihydro*-1 : 2 : 4-*benzotriazine*,  , formed by coupling *o*-*p*-diaminophenol with *p*-diazobenzenesulphonic acid and the product with benzaldehyde; 6-*amino*-3-*phenyl*-2-p-*aminophenyldihydro*-1 : 2 : 4-*benzotriazine*; 6-*amino*-2-p-*sulphophenyl*-3-m-*nitrophenyldihydro*-1 : 2 : 4-*benzotriazine*, , from sulphanilic acid, *m*-phenylenediamine and then *m*-nitrobenzaldehyde; 6-*amino*-2-*phenyl*-3-p-*hydroxyphenyldihydro*-1 : 2 : 4-*benzotriazine*, from *p*-hydroxybenzaldehyde and chrysoidin, and the corresponding *methoxy*-compound from anisaldehyde and chrysoidin; a *triazine* from Bismarck-brown and benzaldehyde; a *ditriazine*,  ; and 6-*amino*-2-m-*carboxyphenyl*-3-*phenyldihydro*-1 : 2 : 4-*benzotriazine*,

from diazotised *m*-aminobenzoic acid and *m*-phenylenediamine and then benzaldehyde. J. C. W.

o-Aldehydophenylglycine. III. A Class of New Derivatives of *o*-Aldehydophenylglycine. WILHELM GLUUD (*Ber.*, 1915, **48**, 425—432. Compare following Abstract, and T., 1913, **103**, 1251). —When a suspension of the sparingly soluble oxime of *o*-aldehydophenylglycinamide is warmed for a short time with an aqueous solution of formaldehyde, a clear solution is obtained, which on cooling gives an almost quantitative deposit of a yellow solid; the formation of this is due to the condensation of equimolecular proportions of the amide and formaldehyde with elimination of a molecule of water. The oxime of *o*-aldehydophenylglycine behaves in a similar manner, and the reaction is not peculiar to formaldehyde, but can be extended to other aldehydes.

Anhydroformaldehydophenylglycinamide-o-aldoxime,

$$NO\cdot CH<\begin{matrix}CH_2\\C_6H_4\end{matrix}>N\cdot CH_2\cdot CO\cdot NH_2,$$

obtained from the oxime of *o*-aldehydophenylglycine-amide and formaldehyde, forms yellow tablets, m. p. 233—234° (decomp.). *Anhydroacetaldehydophenylglycinamide-o-aldoxime*,

$$NO\cdot CH<\begin{matrix}CHMe\\C_6H_4\end{matrix}>N\cdot CH_2\cdot CO\cdot NH_2,$$

m. p. 233°, was obtained in a similar manner by using acetaldehyde. Glyoxal by this reaction gave a *substance*, $C_{11}H_{11}O_3N_3$, yellow, hexagonal columns, m. p. below 100°.

By this same reaction the oxime of *o*-aldehydophenylglycine, when warmed with acetaldehyde, propionaldehyde, benzaldehyde, cinnamaldehyde, and furfuraldehyde respectively, produced *anhydroacetaldehydophenylglycine-o-aldoxime*, $NO\cdot CH<\begin{matrix}CHMe\\C_6H_4\end{matrix}>N\cdot CH_2\cdot CO_2H$, yellow, tetragonal or hexagonal tablets, m. p. near 190° (decomp.), *anhydropropionaldehydophenylglycine-o-aldoxime*, $NO<\begin{matrix}CHEt\\C_6H_4\end{matrix}>N\cdot CH_2\cdot CO_2H$, yellow prisms, m. p. 175° (decomp.), *anhydrobenzaldehydophenylglycine-o-aldoxime*, $NO\cdot CH<\begin{matrix}CHPh\\C_6H_4\end{matrix}>N\cdot CH_2\cdot CO_2H$, yellow needles, m. p. near 204—205° (decomp.), *anhydrocinnamaldehydophenylglycine-o-aldoxime*, $C_6H_4<\begin{matrix}CH(NO)\text{———}\\N(CH_2\cdot CO_2H)\end{matrix}>CH\cdot CH{:}CHPh$, yellow needles, m. p. 166—167° (decomp.), and *anhydrofurfuraldehydophenylglycine-o-aldoxime*, $C_6H_4<\begin{matrix}CH(NO)\text{———}\\N(CH_2\cdot CO_2H)\end{matrix}>CH\cdot C_4H_3O$, tetragonal plates, m. p. 195—197° (decomp.).

Anhydroformaldehydophenylglycine-o-aldoxime was not obtainable in the same manner as the immediately preceding compounds, but was produced by hydrolysis of the corresponding amide derivative (described above) with *N*-sodium hydroxide solution; it forms yellow, rectangular tablets, m. p. near 210° (decomp.). Both this substance and the corresponding amide derivative, when warmed with aqueous sulphurous acid, undergo hydrolysis, yielding *o*-aldehydophenylglycine. D. F. T.

o-Aldehydophenylglycine. II. A New and Rational Indole Synthesis. W. Gluud (*Ber.*, 1915, **48**, 420—425. Compare T., 1913, **103**, 1251).—*o*-Aldehydophenylglycine, $CHO\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO_2H$, should supply a convenient method of approaching the synthesis of indole, but the satisfactory hydrolysis of the oxime first produced (*loc. cit.*) proved more troublesome than was anticipated. It has now been found that aqueous sulphurous acid is an excellent agent for the hydrolysis of oximes, with formation of the corresponding aldehydes in good yield and in a high state of purity. Thus the oxime of *o*-aldehydophenylglycine treated with saturated sulphurous acid solution at water-bath temperature for three hours gives an almost 90% yield of *o*-aldehydophenylglycine. In a similar manner, oximinocamphor in twenty-four hours gives a 50% yield of camphorquinone.

The condensation of *o*-aldehydophenylglycine to indole is easily effected by heating for ten minutes with acetic anhydride and sodium acetate, when carbon dioxide and water are eliminated, with formation of indole, which can be separated in approximately 80% yield.

The following derivatives of *o*-aldehydophenylglycine are described: *phenylhydrazone*, almost colourless plates, m. p. near 217°, (decomp.); *calcium* salt, yellow; *copper* salt, yellowish-brown; *cobalt* salt, yellow; *mercury* salt, reddish-yellow; *ferrous* salt, yellow; *ferric* salt, brownish-yellow; *silver* salt, yellow; *barium* salt, yellow.

o-Aldehydophenylglycine was also produced by the hydrolysis of the oxime of *o*-aldehydophenylglycinamide with aqueous sodium hydrogen sulphite solution, with subsequent removal of the sulphite by heating with dilute sulphuric acid. D. F. T.

Aromatic Selenium Compounds. IV. *o*-Selenocyanobenzoic Acid. R. Lesser and A. Schoeller (*Ber.*, 1914, **47**, 2505—2510. Compare A., 1914, i, 1083; Lesser and Weiss, A., 1913, i, 1184; 1912, i, 642).—Diphenyldiselenidedi-*o*-carboxylic acid (Lesser and Weiss, A., 1913, i, 1184) has been found to be converted by thionyl chloride into a substance $C_{14}H_{10}O_2Cl_4Se_2$, described as the hydrochloride of the corresponding acid chloride, and the subsequent reactions of the new product have been interpreted in the same light. The action of silver cyanide on an equimolecular proportion of the fused chlorine compound, however, gives rise to an acid chloride, from which on treatment with methyl alcohol, methyl *o*-selenocyanobenzoate is obtained. The earlier view as to the nature of the chlorine compound was therefore erroneous, and the product of the action of thionyl chloride on diphenyldiselenidedi-*o*-carboxylic acid is in reality *o-chloroselenolbenzoyl chloride*, $SeCl\cdot C_6H_4\cdot COCl$, a selenium analogue of the chlorothiol compounds discovered by Zincke (A., 1911, i, 368); with the use of pure thionyl chloride no concurrent formation of the chloride of diphenyldiselenidedi-*o*-carboxylic acid occurs. The chloroselenol chloride differs markedly from the chlorothiol compounds by the inactivity of its chloroselenol group towards alcohols; treatment with ethyl and methyl alcohols produces respectively *ethyl* and *methyl* o-*chloroselenolbenzoates* (compare *loc. cit.*).

o-*Selenocyanobenzoyl chloride* forms pale yellow leaflets or broad

needles, m. p. 122—123°; when boiled with methyl alcohol it gives *methyl* o-*selenocyanobenzoate*, colourless needles, m. p. 114—115°, which can also be obtained by the interaction of potassium selenocyanate and a diazotised solution of methyl anthranilate; the corresponding *ethyl* ester forms prisms, m. p. 125—126°. o-*Selenocyanobenzoic acid*, produced by the action of dilute sodium carbonate solution on the chloride, forms colourless leaflets, m. p. 185° (decomp.); *barium* salt, needles; *ferric* salt, brown; *silver* salt, colourless; *copper* salt, blue. When treated with hydrogen chloride a methyl-alcoholic solution of the acid gives methyl diphenyldiselenidedi-*o*-carboxylate in place of the expected ester.

In the interaction of silver cyanide and the chloride of diphenyldiselenidedicarboxylic acid, a *compound*, C_8H_5ONSe, leaflets, m. p. 235°, was obtained, of which the nature is at present uncertain.

D. F. T.

Thiocarbamide-Phenylpropiolic Acid and β-Thiolcinnamic Acid. Emil Fischer and Walter Brieger (*Ber.*, 1914, **47**, 2469—2478).—When phenylpropiolic acid and thiocarbamide are heated together in boiling acetone for twenty-five hours, an additive compound, $C_{10}H_{10}O_2N_2S$, is formed; the same substance is obtained, but in a less pure condition, by mere fusion of a mixture of the components. The product, which is designated *thiocarbamide-phenylpropiolic acid* after its constituents, forms microscopic crystals of tetragonal cross-section, m. p. 188—191° with decomposition, which actually commences near 172°; it is sparingly soluble in the usual solvents with the exception of mineral acids with which it forms salts; the *sulphate*, long needles, regenerates the base on addition of sodium hydrogen carbonate.

When treated with cold dilute alkalis, for example, *N*-sodium hydroxide solution, the additive compound passes into solution with decomposition, and the liquid on acidifying deposits *β-thiolcinnamic acid*, $SH\cdot CPh{:}CH\cdot CO_2H$, whilst the solution retains dicyanodiamide, resulting from the primarily produced cyanoamide. The acid forms inodorous, very pale yellow needles, m. p. 110° (decomp.) with incipient decomposition at 98°; it is not very stable, and on keeping acquires an unpleasant odour; *silver* salt, yellow; *lead* salt, yellow; *copper* salt, dark brown; with a little ammonia and ferric chloride solution, a suspension of the acid gives a coloration ranging from blue to brown according to the concentration. The constitution of this acid is proved by the considerable yield of benzoic acid on its oxidation with sulphuric acid and potassium dichromate, and its formation from the above additive compound suggests the structure

$$NH{:}C(NH_2)\cdot S\cdot CPh{:}CH\cdot CO_2H$$

for the latter.

Oxidation of the above β-thiolcinnamic acid with iodine in carbon disulphide solution produces pale orange-coloured leaflets of *β-disulphidocinnamic acid*, $S_2(CPh{:}CH\cdot CO_2H)_2$, m. p. near 155° (decomp.) after previously sintering at 140°; *barium* and *calcium* salts, yellow; *silver* salt, brown; *copper* salt, green; *ferric* salt, brown.

Reduction of β-thiolcinnamic acid in aqueous suspension by sodium

amalgam yielded *β-thiol-β-phenylpropionic acid*, $SH\cdot CHPh\cdot CH_2\cdot CO_2H$, colourless leaflets, m. p. 111·5—112·5° (corr.); *calcium* and *barium* salts, soluble; *silver* salt, colourless. This acid, on oxidation by ferric chloride in aqueous solution, gave *β-disulphido-β-phenylpropionic acid*, $S_2(CHPh\cdot CH_2\cdot CO_2H)_2$, m. p. 146—147°, which in alcoholic solution with silver nitrate gives a colourless, amorphous precipitate which turns yellow on warming.

The properties and derivatives of the β-thiolcinnamic acid described above prove it to be quite distinct from the thiolcinnamic acid already prepared by Bondzyński (A., 1887, 1108), which must therefore be α-thiolcinnamic acid. This acid on reduction under the same conditions as with its β-isomeride produces *α-thiol-β-phenylpropionic acid*,

$$CH_2Ph\cdot CH(SH)\cdot CO_2H,$$

m. p. 48—49° (*silver* salt, colourless), which is oxidisable by ferric chloride solution to a yellow viscous oil, presumably *α-disulphido-β-phenylpropionic acid*. D. F. T.

Photochemistry of Stilbene and of Ethyl Phenylitaconate. Hans Stobbe (*J. pr. Chem.*, 1914, [ii], **90**, 551—554).—The behaviour of stilbene and ethyl γ-phenylitaconate under the influence of light is compared with that of styrene and ethyl itaconate (this vol., i, 213, 261). In light of short wave-length stilbene undergoes auto-oxidation (compare Ciamician and Silber, A., 1904, i, 161) and in ultraviolet light isomerisation (compare Stoermer, A., 1910, i, 114). Whether polymerisation also occurs was not decided in either case, but experiments now being carried out by the author indicate that spontaneous polymerisation is slow and imperfect. Styrene, on the other hand, shows marked readiness to polymerise, and, under the influence of sunlight, is decomposed into benzaldehyde and formaldehyde. Thus, with stilbene auto-oxidation predominates, and with styrene, polymerisation.

When ethyl γ-phenylitaconate is kept for five months in the dark, its molecular weight in boiling benzene rises to a value corresponding with the formula $(C_{15}H_{18}O_4)_4$, and, after a similar exposure in the light, the formula is apparently $(C_{15}H_{18}O_4)_6$. In either case, however, the product probably represents a solution of still higher polymerides in the monomeric ester. Under the action of light the refractive index, n_C^{20}, falls from 1·52429 to 1·52204 after 145 days, and in the dark, to 1·52394 after 147 days. It is evident that the ester of γ-phenylitaconic acid undergoes change far more slowly than that of itaconic acid, which, after an exposure of three months to light, has a molecular weight of such magnitude that it cannot be determined (this vol., i, 213). In the latter case, the refractive index increases as polymerisation proceeds, so that the two modes of polymerisation are structurally different. T. H. P.

Configuration of the Stereoisomeric Diphenylsuccinic Acids. Henry Wren and Charles James Still (T., 1915, **107**, 444—451).—This investigation was undertaken with a view to the determination of the configuration of the symmetrical diphenylsuccinic acids, and it has been found that β-diphenylsuccinic acid is the *meso*-form and α-diphenylsuccinic acid the racemic form. The latter has been resolved

into its optically active components by the fractional crystallisation of the brucine salt. Attempts were also made to resolve the β-acid by means of morphine and brucine, but although crystalline salts were formed, an optically active acid could not be obtained.

The most convenient method of preparing ethyl α- and β-diphenylsuccinate is by the interaction of ethyl phenylacetate and iodine in dry ethereal solution in presence of solid sodium ethoxide. The esters of the α- and β-acids have m. p. 82—83·5° (corr.) and 140—141° (corr.) respectively. α-Diphenylsuccinic acid melts at 183°, afterwards re-solidifies, and then melts at 220—221°; the β-acid has m. p. 229—230°.

d-*Diphenylsuccinic acid* crystallises in minute needles; when heated, it melts at 179—180°, re-solidifies, and subsequently melts at 212—214°; it has $[\alpha]_D^{14}$ + 397·9° in acetone solution and $[\alpha]_D^{16\cdot5}$ +369·7° in alcoholic solution. l-*Diphenylsuccinic acid* melts at 176—177°, resolidifies, and then melts at 211·5—214°; it has $[\alpha]_D^{13}$ −368·9° in alcoholic solution. Attempts to effect the resolution of α-diphenylsuccinic acid by means of quinine, cinchonine, strychnine, or morphine, instead of brucine, were not successful. E. G.

Preparation of 1-Aminoanthraquinone-2-carboxylic Acids and their Derivatives. Badische Anilin- & Soda-Fabrik (D.R.-P. 279867; from *J. Soc. Chem. Ind.*, 1915, **34**, 347. Compare A., 1912, i, 979).—Condensations in the β-aminoanthraquinone series may be effected without the addition of copper or copper compounds. J. C. W.

Preparation of Anthracene-1 : 9-dicarboxylic Acid and its Substitution Products. Badische Anilin- & Soda-Fabrik (D.R.-P. 280092; from *J. Soc. Chem. Ind.*, 1915, **34**, 347).—Aceanthrenequinone or one of its substitution products is oxidised by a mild agent, such as manganese dioxide or permanganate in neutral or alkaline aqueous suspension or solution, or with the required amount of sodium dichromate and glacial acetic acid. Aceanthrenequinone itself yields anthracene-1 : 9-dicarboxylic acid and anthraquinone-1-carboxylic acid, which are easily separated. J. C. W.

Action of Magnesium on Esters of Halogen-substituted Aromatic Acids. J. Zalkind and A. A. Schmidt (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 681—687).—It has been previously found that the esters of all halogenated aromatic acids containing both the halogen and the carboxyl group in the side-chain react with magnesium, although with esters of β-halogenated acids it is sometimes necessary to activate the magnesium (A., 1914, i, 958, 959, 960, 961). When, however, both the halogen and the carboxyl group are united directly to the nucleus, their combined effect results in a marked diminution in the capacity of the bromine atom to react with magnesium (*loc. cit.*; Meyer and Tögel, A., 1906, i, 757).

The bromine atom is rendered slightly more mobile by the transference of the carboxyl group to the side-chain. Thus, whilst ethyl *p*-bromophenylacetate does not react with magnesium, ethyl *p*-bromo-

β-phenylpropionate is somewhat less inert and ethyl *o*-bromophenylacetate is able to react, although with difficulty. When, instead of the carboxyl group, the bromine atom is in the side-chain, the esters exhibit increased activity towards magnesium; here, too, the para-derivatives are inactive, but ethyl ω-bromo-*o*- and -*m*-toluates are able to react with magnesium. In the latter cases, just as with esters of β-halogenated acids (A., 1914, i, 960), a large proportion of the organomagnesium compound first formed reacts further, three molecules undergoing condensation with formation of a dibasic hydroxy-acid. Consequently, with all those esters of halogenated acids in which the halogen is further from the carboxyl group than it is when it occupies the α-position, the course of the reaction is expressed by the general scheme given for the β-halogenated esters (*loc. cit.*).

The action of magnesium, activated by means of iodine, on ethyl ω-bromo-*o*-toluate in presence of ether, followed by decomposition of the product with water, yields: (1) ethyl *o*-toluate in small proportion, and (2) the ethyl ester of *β-hydroxy-β-o-tolyl-αγ-di-o-carboxyphenylpropane*, $C_6H_4Me\cdot C(OH)(CH_2\cdot C_6H_4\cdot CO_2H)_2$, which forms amorphous, yellow drops and has the normal molecular weight in boiling ether; its *silver* salt and the *silver* salt of its *acetyl* derivative, $C_{26}H_{22}O_6Ag_2$, were analysed.

β-Hydroxy-β-m-*tolyl-αγ-di*-m-*carboxyphenylpropane*,

$$C_6H_4Me\cdot C(OH)(CH_2\cdot C_6H_4\cdot CO_2H)_2,$$

similarly obtained from ethyl ω-bromo-*m*-toluate, forms white, amorphous flocks turning yellow at 250° and decomposing at 280°, and exhibits normal ebullioscopic behaviour in acetone; its *silver* salt and that of its *acetyl* derivative were analysed. When oxidised by means of permanganate, it yields (1) *ω-m-toluoyl-m-toluic acid*,

$$C_6H_4Me\cdot CO\cdot CH_2\cdot C_6H_4\cdot CO_2H,$$

which is amorphous and decomposes, without melting, at about 240°; its *silver* salt was analysed; and (2) probably ω-hydroxy-*m*-toluic acid, which was not, however, isolated. T. H. P.

Asymmetric Synthesis of Mandelic Acid; Formation of Ethyl Benzylidenetartrate and Benzylidenetartaric Acid. Emil Erlenmayer [with G. Hilgendorf] (*Biochem. Zeitsch.*, 1914, **68**, 351—367).—Attention is called to the fact that when benzaldehyde is heated in alcoholic solution with *d*-tartaric acid only a very small part of the aldehyde is converted into an optically active form. Nevertheless, the alcoholic solution undergoes considerable change in its rotation. It is now shown that this is due to the formation of *benzylidenetartaric* [*benzylidenedioxysuccinic*] *acid* and its *ethyl* ester. The excess of tartaric acid is separated from the solution by the addition of ether and water, and the tartrate and ester then remain in the alcoholic solution. The benzylidenedioxysuccinate is separated from the ester by extraction with sodium hydrogen carbonate, and the aldehyde is removed from the former substance by distillation in a vacuum and steam distillation. The ester, $C_{15}H_{18}O_6$, m. p. 48—49°, $[\alpha]_D = -40°$, is soluble in light petroleum. The free acid was not obtained pure, as it readily decomposes in moist air into benzaldehyde and tartaric acid. Nevertheless, it can be obtained from its ester by

hydrolysis with alkalis; the sodium salt appears to be more stable than the free acid. S. B. S.

Manufacture of Selenofluoresceins. C. JÄGER, G.m.b.H., and R. W. CARL (D.R.-P. 279549; from *J. Soc. Chem. Ind.*, 1915, **34**, 274).—Good yields of derivatives analogous to the thiofluoresceins are obtained by treating fluorescein or its halogen compounds with selenium, in alkaline solution. The products may be useful therapeutically, but not as dyes. J. C. W.

Phthalylglycyl Chloride and Ethyl Sodiomalonate. S. GABRIEL (*Ber.*, 1914, **47**, 2919—2922).—The compound described by Weizmann, Stephen, and Agashe (T., 1913, **103**, 1855), produced by the condensation of phthaliminoacetyl chloride and ethyl sodiomalonate, and considered to be the ketonic form of ethyl phthaliminoacetoacetate, m. p. 119°, is *ethyl γ-diphthaliminoacetomalonate*, m. p. 118—119°, which gives no coloration with ferric chloride. The so-called enolic form produced by the action of potassium ethoxide, m. p. 70°, is *ethyl γ-phthalimino-β-ketopropanedicarboxylate*,

$$C_8H_4O_2N\cdot CH_2\cdot CO\cdot CH(CO_2Et)_2,$$

m. p. 68—68·5°, identical with Pfähler's compound (A., 1913, i, 750).

Saponification of ethyl phthaliminoacetoacetate with sulphuric acid yields *phthaliminoacetoacetic acid*, $C_8H_4O_2N\cdot CH_2\cdot CO\cdot CH_2\cdot CO_2H$, needles, m. p. 123—124° (decomp.). Saponification with sodium hydroxide produces *ethyl phthaloylaminoacetoacetate*

$$CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot CH_2\cdot CO_2Et,$$

needles, m. p. 108·5—109°. A. J. W.

Action of Aldehydes on the Grignard Reagent. II. JOSEPH MARSHALL (T., 1915, **107**, 509—523).—In an earlier paper (T., 1914, **105**, 527) it was stated that when benzaldehyde (2 mols.) was added to magnesium methyl iodide (1 mol.), methyldeoxybenzoin was produced, but it is now shown that the product was not methyldeoxybenzoin, but consisted of phenyl styryl ketone contaminated with a small quantity of dibenzoylmethane. It has been found that an excess of benzaldehyde reacts similarly with magnesium dimethylcarbinyl iodide with formation of styryl methyl ketone as the chief product. Similar results are also obtained by the action of excess of an aliphatic aldehyde on magnesium carbinyl haloids. Thus, when an excess of acetaldehyde reacts with magnesium phenyl bromide, acetophenone and benzoylacetone are produced. These results may be explained on the assumption that the excess of the aldehyde present is capable of acting as an oxidising agent, being itself reduced to a primary alcohol.

Sabatier and Murat (A., 1914, i, 168) have found that when benzaldehyde reacts with magnesium phenyl bromide, only 3% of diphenylcarbinol is produced, the chief product obtained being tetraphenylethane, which is accompanied by diphenylmethane and benzophenone. It is now shown that the formation of tetraphenylethane is due to the presence of undissolved magnesium in the reaction mixture, and that, during the hydrolysis, this effects the reduction of diphenyl-

carbinol (or, more probably, magnesium diphenylcarbinyl bromide) to tetraphenylethane or diphenylmethane. If the excess of metal is removed before the aldehyde is added, the yield of diphenylcarbinol (or benzophenone) is more than 50% of the theoretical, whilst if, on the other hand, a large excess of magnesium is left in contact with the reaction mixture, a yield of tetraphenylethane, amounting to 45%, can be obtained, the fraction containing the diphenylcarbinol and benzophenone being diminished to less than 10%.

An experiment was made to ascertain whether an excess of magnesium would similarly effect the formation of hexaphenylethane from benzophenone and magnesium phenyl bromide, but the only product obtained was triphenylcarbinol.

Benzaldehyde (1 mol.) and magnesium *p*-tolyl iodide (1 mol.) yield phenyl-*p*-tolylcarbinol as the principal product, whilst when 2 mols. of benzaldehyde are used, benzyl alcohol and phenyl *p*-tolyl ketone are produced; di-*p*-tolyl is also formed in each case.

The reaction between benzaldehyde ($1\frac{1}{2}$ mols.) and magnesium ethyl iodide (1 mol.) yields benzyl alcohol, phenylethylcarbinol, propiophenone, and dibenzoylethane. 1 : 3 : 5-*Triphenyl*-4-*methylpyrazole*, m. p. 125°, produced by the action of phenylhydrazine on dibenzoylethane, forms colourless, silky needles. 3 : 5-*Diphenyl*-4-*methyl*isoxazole, m. p. 127°, obtained by boiling a solution of dibenzoylethane in dilute alcohol with hydroxylamine hydrochloride, crystallises in lustrous plates. *Bromodibenzoylethane*, m. p. 65°, forms colourless prisms.

Benzaldehyde and magnesium propyl iodide react with production of dibenzoylpropane, m. p. 87°. *Bromodibenzoylpropane*,

COPh·CBrEt·COPh,

m. p. 52°, crystallises in hexagonal prisms. 1 : 3 : 5-*Triphenyl*-4-*ethylpyrazole*, m. p. 84—85°, forms colourless needles.

When benzaldehyde is added to magnesium *iso*propyl iodide, phenyl-*iso*propylcarbinol and phenyl *iso*propyl ketone are produced, together with a small quantity of a yellow, crystalline substance, m. p. 110°.

The reaction between benzaldehyde and magnesium benzyl bromide results in the formation of phenylbenzylcarbinol and dibenzoylphenylmethane together with dibenzyl and phenyl benzyl ketone. *Dibenzoylphenylmethane*, m. p. 149°, crystallises in colourless needles; its *bromo*-derivative, m. p. 147°, forms colourless prisms. *Dibenzoylphenylmethaneoxime*, m. p. 153°, crystallises in slender needles, and when heated above its m. p. is converted into 3 : 4 : 5-*triphenyl*isooxazole, m. p. 212°.

Acetaldehyde and magnesium phenylmethylcarbinyl bromide yield acetophenone, benzoylacetone, and small quantities of another substance, probably phenyl propenyl ketone. Acetaldehyde and magnesium *iso*propyl iodide give acetone, *iso*propyl alcohol, and a little ethylideneacetone.

By the action of benzaldehyde on magnesium diphenylmethylcarbinyl bromide, diphenylmethylcarbinol and dibenzoylmethane are produced.

Ethyl acetate reacts with magnesium phenylmethylcarbinyl iodide with formation of phenylmethylcarbinyl acetate. E. G.

[Stereochemical Treatment of the Keto–Enol Question.] HERMANN LEUCHS (*Ber.*, 1914, **47**, 2528—2530).—A reply to Meyer's criticism (A., 1914, ii, 351) of the author's conclusions (A., 1913, i, 974). D. F. T.

Isomeric Transformations of Cyclic α-Monochloroketones. AL. FAVORSKI and V. BOSHOVSKI (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1097—1102).—It has been shown previously (A., 1893, i, 391) that, in an alkaline medium, unsymmetrical α-dichloroketones with open carbon-atom chains undergo transformation, giving acids of the acrylic series. It is now found, as was to be expected, that cyclic α-chloroketones are similarly affected by alcoholic potassium hydroxide solution, the products being cyclic acids with the number of carbon atoms in the ring diminished by one. These reactions are simultaneously reductions and oxidations, and it is supposed that the initial products have the structure of carbonylic hydrates, which lose the elements of hydrogen chloride in presence of potassium hydroxide, the resulting unstable hydroxylic oxides or chlorinated hydroxylic oxides then undergoing isomerisation into acids:

$$\begin{array}{l}\mathrm{C\cdot C\cdot CHCl}\\ \mathrm{C\cdot C\cdot C(OH)_2}\end{array} \longrightarrow \begin{array}{l}\mathrm{C\cdot C\cdot CH}\text{—}\\ \mathrm{C\cdot C\cdot C(OH)}\end{array}\!\!>\mathrm{O} \longrightarrow \begin{array}{l}\mathrm{C\cdot C}\\ \mathrm{C\cdot C}\end{array}\!\!>\mathrm{CH\cdot CO_2H}.$$

Thus, the carboxyl group is formed always at that carbon atom to which the chlorine is united in the chloro-ketone, and the structure of the latter will, in general, determine that of the acid; when, however, an acid of the acrylic acid series is formed, its structure will depend on the mode in which hydrogen chloride is lost from the intermediate saturated chloro-acid.

2-Chloro*cyclo*hexanone and alcoholic potassium hydroxide react vigorously, giving *cyclo*pentanecarboxylic acid.

When chlorinated in presence of water and excess of calcium carbonate, 1-methyl*cyclo*hexan-3-one yields a chloro-1-methyl*cyclo*hexan-3-one, m. p. 55—56°, and a dichloro-1-methyl*cyclo*hexan-3-one, m. p. 93—93·5°. These results differ from those of Kötz and Steinhorst (A., 1911, i, 210), who obtained two monochloro-derivatives, one liquid, b. p. 96—98°/12 mm., and the other solid, m. p. 61—62°. Since chlorination of ketones invariably results in the introduction of the chlorine atom in a position adjacent to that of the carbonyl group, the authors' monochloro-ketone must be structurally identical with Kötz's products and thus contain the chlorine atom in the para-position to the methyl group or must contain the chlorine atom in the ortho-position to both the methyl and the carbonyl groups. It is found that the action of alcoholic potassium hydroxide (2·5 mols.) on chloro-1-methyl*cyclo*hexan-3-one (1 mol.), m. p. 55—56°, yields an acid having the properties of methyl*cyclo*pentane-3-carboxylic acid (compare Euler, A., 1896, i, 145). The conclusion is drawn that the chloro-ketone is 4-chloro-1-methyl*cyclo*hexan-3-one. T. H. P.

Action of Sodamide on the Dialkylallylacetophenones. II. Preparation of 2 : 4-Dimethyl-4-ethyl- and 2-Methyl-4 : 4-diethyl-5-pyrrolidones. A. HALLER and ÉDOUARD BAUER (*Compt. rend.*, 1915, **160**, 541—543).—The behaviour of dimethylallylacetophenone towards sodamide, yielding a pyrrolidone derivative (compare

A., 1914, i, 724), is apparently general to all dialkylallylacetophenones. In this way methylethylallylacetophenone with sodamide in boiling benzene yields 2 : 4-*dimethyl*-4-*ethyl*-5-*pyrrolidone*,

$$NH\begin{cases}CO---CMeEt\\ |\\ CHMe\cdot CH_2\end{cases},$$

m. p. 82°, b. p. 134—136°/16 mm. Similarly, diethylallylacetophenone yields 2-*methyl*-4 : 4-*diethyl*-5-*pyrrolidone*, $NH\begin{cases}CO---CEt_2\\ |\\ CHMe\cdot CH_2\end{cases}$, m. p. 49—50°, b. p. 144—146°/16 mm. Both of these products are soluble in water, alcohol, ether and benzene, and neither decolorises bromine water.

On ascending this series of pyrrolidones from 2 : 4 : 4-trimethyl-5-pyrrolidone (*loc. cit.*), their boiling points, under the same pressure, increase 10° with each addition of $\cdot CH_2\cdot$ to the molecule, whilst the melting points diminish but irregularly. W. G.

Reactions of Dimethylphenacetoxime (*m*-4-Xylyl Methyl Ketoxime). N. ISHIZAKA (*Ber.*, 1914, **47**, 2460—2462).—m-4-*Xylyl methyl ketoxime*, $C_6H_3Me_2\cdot C(:NOH)\cdot CH_3$, needles, m. p. 63—64°, b. p. 153—155°/15 mm., was prepared from the corresponding ketone, which is producible by the condensation of acetyl chloride with *m*-xylene in the presence of aluminium chloride. Reduction of the oxime with sodium and alcohol gave rise to α-m-4-*xylylethylamine*, $C_6H_3Me_2\cdot CHMe\cdot NH_2$, b. p. 110—112°/15 mm., in theoretical yield; the new base gives a *hydrochloride*, m. p. 162—163°, and an *acetyl* derivative, m. p. 101—102°. When treated in 15% acetic acid solution with sodium nitrite, the base was converted into α-m-4-*xylylethyl acetate*, $C_6H_3Me_2\cdot CHMe\cdot OAc$, which on hydrolysis gave α-*m*-4-xylylethyl alcohol, b. p. 124—125°/14 mm.

When submitted to the Beckmann rearrangement, the oxime yielded aceto-4-*m*-xylidide, $C_6H_3Me_2\cdot NHAc$, leaflets, m. p. 129—130° (Willgerodt and Schmierer, A., 1905, i, 425). D. F. T.

Doebner's Benzoylcatechol [1 : 2-Hydroxybenzophenone]. NIK. ROSHDESTVENSKI (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1075—1077).—Doebner (A., 1882, 508) stated that this compound, $COPh\cdot C_6H_3(OH)_2$, crystallises with $\frac{1}{2}H_2O$, and has m. p. 145°, whereas Bartolotti (A., 1897, i, 566) found $1H_2O$ and m. p. 134°. The author has prepared it, together with benzoic acid, by heating a mixture of catechol, benzoic anhydride, and zinc chloride at 180°: $O(COPh)_2 + C_6H_4(OH)_2 = COPh\cdot C_6H_3(OH)_2 + Ph\cdot CO_2H$. When placed in a desiccator over sulphuric acid, the compound loses any water of crystallisation in a few days, the m. p. of the anhydrous compound being 134°. It readily yields a yellow solution with dilute, and a bright orange one with concentrated, alkali hydroxide solution; with ferric chloride it gives a dark green coloration. T. H. P.

Alkyl Ethers of Some Oximes. I, II, and III. LUIGI ALESSANDRI (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 129—135, 216—221, 257—262. Compare Angeli, Alessandri and Aiazzi-Mancini, A., 1911, i, 544).—*Benzophenoneoxime O-benzyl ether*, $C_{20}H_{17}ON$

(from the silver salt of the oxime and benzyl iodide), forms colourless, prismatic or acicular crystals, m. p. 58° (compare Spiegler, A., 1884, 1155). The structure of the substance is shown by the production of α-benzylhydroxylamine and benzophenone on hydrolysis. When instead of the silver salt the sodium salt of benzophenoneoxime is used for the reaction the same ether is obtained, but, in addition, the N-*benzyl ether*, $C_{20}H_{17}ON$, which forms prismatic crystals, m. p. 119°, and yields on hydrolysis β-benzylhydroxylamine and benzophenone.

β-Diphenylmethylhydroxylamine condenses with benzaldehyde yielding the N-*diphenylmethyl ether* of *benzaldoxime*, $CHPh_2 \cdot NO{:}CHPh$, which crystallises in needles, m. p. 159°, and is identical with the oxidation product of benzyldiphenylmethylhydroxylamine of this m. p. obtained by Angeli, Alessandri and Aiazzi-Mancini (*loc. cit.*).

The silver salt of benzophenoneoxime and methyl iodide yield the O-*methyl ether*, m. p. 60°. This was identified by reduction to diphenylmethylamine. Using the sodium salt instead of the silver salt, Spiegler obtained (*loc. cit.*) an ether of m. p. 92°, whilst Ponzio and Charrier obtained an ether of m. p. 102°. The author finds that in this reaction three substances are produced: (1) the above *O*-methyl ether, m. p. 60°; (2) the *N*-methyl ether, m. p. 103° (identified by hydrolysis to β-methylhydroxylamine and benzophenone); (3) a product, m. p. 108°, formed by the union of equimolecular quantities of benzophenoneoxime and its *N*-methyl ether.

β-Diphenylmethylamine, $CHPh_2 \cdot NH_2$, yields a *benzoyl* derivative, m. p. 172°, and a *picrate*, m. p. 202° (with evolution of gas).

The *N*-alkyl ethers of benzophenoneoxime are decomposed by light, whilst the *O*-ethers are not. R. V. S.

Elimination of Bromine from Dibromoanisylideneacetophenone. F. J. Wilson and A. Archibald Boon (*Pharm. J.*, 1915, **94**, 486—487).—The authors have attempted to study the rate of the replacement of bromine by alkyloxyl, which such a compound as the dibromide of piperonylidenepinacolin, $C_7H_5O_2 \cdot CHBr \cdot CHBr \cdot CO \cdot CMe_3$, suffers when boiled with alcohols (T., 1910, **97**, 1752). They have chosen for examination the more simple dibromoanisylideneacetophenone, $OMe \cdot C_6H_4 \cdot CHBr \cdot CHBr \cdot COPh$ (Pond, Maxwell and Norman, A., 1900, i, 102; 1901, i, 35), but have not attained the object in view.

The above dibromide readily exchanges one bromine atom for alkyloxyl when boiled for a few minutes with methyl or ethyl alcohol (*ibid.*). It is also converted into monobromoanisylideneacetophenone when boiled for a few hours with propyl, *iso*butyl or benzyl alcohol, or glacial acetic acid, and into anisylideneacetophenone when boiled with *iso*propyl or *tert.*-butyl alcohol, or acetone or benzoin, the by-products being somewhat obscure. The authors cited above had effected these changes by means of the required quantities of sodium alkyloxides. J. C. W.

Action of Hydrochloric Acid and Formaldehyde on Oximino-α-hydrindone and Its 3-Methyl Derivative. Wilhelm Steinkopf and Rista Bessaritsch (*Ber.*, 1914, **47**, 2925—2931. Compare Perkin, Roberts, and Robinson, T., 1912, **101**, 232; von Braun and Kirschbaum, A., 1913, i, 1363).—When excess of hydro-

chloric acid is employed in the preparation of 1 : 2-diketo-3-methylhydrindene from oximino-3-methylhydrindone, the product is not the viscous red oil described by von Braun and Kirschbaum, but two crystalline, colourless *compounds* with the formulæ $C_9H_8O_2$ and $C_9H_{10}O_3$. Their constitution has not been elucidated, but both have one carbon atom more than the parent substance, and the second substance contains H_2O more than the first. Both substances dissolve in alkalis to deep violet solutions, the colour of which gradually changes to muddy yellow. These alkali solutions yield the same *dibenzoyl* derivative, $C_9H_8(OBz)_2$, indicating the presence of the same carbon nucleus. On oxidation the substance $C_9H_8O_2$ yields phthalic acid, proving it to be an *o*-di-derivative of benzene. With *o*-phenylenediamine the compound $C_9H_{10}O_3$ yields by condensation a *substance* containing nitrogen. With thiophen and sulphuric acid both substances give an intense indophenin reaction. The oil obtained by von Braun and Kirschbaum is probably a mixture of several substances. For the m. p. of oximinomethylhydrindone and that of its benzoyl derivative these authors give 130° and 125°. On slow heating the oximino-compound shrinks at 100—105°, and most of it melts at 115—118°. Rapid heating causes shrinking at 132°, the substance melting at 135°. The benzoyl derivative has m. p. 127—128°.

The *compound*, $C_9H_8O_2$, forms lustrous, prismatic crystals, m. p. 170—172°. From its solution in alkali after disappearance of the violet colour, hydrochloric acid precipitates a crystalline *substance*, m. p. 220° (decomp.). After the lapse of two to three weeks, the mother liquor of the substance $C_9H_8O_2$ deposits the *substance* $C_9H_{10}O_3$, slightly red crystals, m. p. 119—120°. The *dibenzoyl* derivative, obtained from both substances, forms golden-yellow crystals, m. p. 110—111°.

The preparation of 1 : 2-diketohydrindene by the method of Perkin, Roberts, and Robinson necessitates the employment of a small proportion of hydrochloric acid. With excess of this acid, the products are wholly different, among them being a *substance*, $C_8H_6O_2$, colourless, refractive needles, m. p. 183—184°. With alkalis it yields a violet solution; concentrated sulphuric acid produces a green solution, the colour being unaltered by addition of thiophen. A. J. W.

Transformations in the Group of the Acetylnaphthols [Hydroxynaphthyl Methyl Ketones]. Otto N. Witt and Otto Braun (*Ber.*, 1914, **47**, 3216—3232).—The three acetyl-α-naphthols which have been described in the literature are reviewed. The first to be prepared was the 3-derivative, m. p. 173—174°, obtained by the condensation of benzylidenelævulic acid (Erdmann, A., 1888, 488). The one obtained originally by the action of glacial acetic acid and zinc chloride on α-naphthol (Witt, A., 1888, 486) has been confirmed by its application in syntheses as 2-acetyl-α-naphthol [1-hydroxy-β-naphthyl methyl ketone]. The failure of the indophenol reaction presented the only difficulty in assuming the presence of a free para-position, but it is now shown that this is merely a matter of choosing the right oxidising agent, for ammoniacal silver oxide produces the desired effect. The remaining surprise, namely, that the acetyl group

should enter the ortho-position in preference to the para, is explained by recognising that the primary product is really α-naphthyl acetate, which undergoes subsequent rearrangement. As a practical result, the yield of 2-acetyl-α-naphthol has been increased to 80% by using acetic anhydride in addition to the acetic acid and zinc chloride.

Two curious facts were observed on recrystallising the crude, apple-green ortho-compound, m. p. 101—103°. Firstly, the colour was sometimes darker, sometimes paler and, secondly, the m. p. gradually sank to 98—99°, the alterations being due, no doubt, to the existence of two tautomerides, one yellow, the other colourless. The latter m. p. was recorded by Gattermann for the pale yellow acetylnaphthol which he obtained by the hydrolysis with aluminium chloride (A., 1893, i, 152) of the unquestioned 4-acetyl-α-naphthyl ethyl ether which he had prepared by the Friedel-Craft's reaction (A., 1890, 962). Gattermann naturally assigned the para-configuration to this acetyl-α-naphthol, but the colour and low m. p. are against this. It is now shown that the compound is, indeed, the older ortho-derivative, although Gattermann's ethyl and methyl ethers were well crystallised, whereas the ethers of 2-acetyl-α-naphthol are oils.

The explanation was found when the Friedel-Craft's reaction, as carried out by Gattermann in carbon disulphide, was repeated. The product was dissolved in ether and exhausted, first by sodium carbonate which removed the true 4-acetyl-α-naphthol, m. p. 198°, and also a diacetyl-α-naphthol, m. p. 140°, then with dilute sodium hydroxide which extracted α-naphthol, leaving in the ethereal layer the 4-acetyl-α-naphthyl ethyl ether, m. p. 78—79°. This showed that aluminium chloride, under casual conditions, may not only hydrolyse the ether, but even disrupt it to α-naphthol and then cause the re-introduction of an acetyl group into the 2- or 4-position with respect to this, or even of two acetyl groups. By moderating the reaction, using benzene instead of carbon disulphide, the 4-acetyl ether has been obtained in a better yield and the hydrolysis of this, in the same medium, has led to a 80% yield of the genuine 4-acetyl-α-naphthol. The high m. p., the lack of colour, the formation of typical *o*-azo-dyes and of phthalic acid, confirm the constitution. Similarly, the facts that the above diacetyl-α-naphthol yields phthalic acid on oxidation and does not react with diazonium salts lead to the 2 : 4-configuration.

4-*Acetyl-α-naphthol* [4-*hydroxy-α-naphthyl methyl ketone*], $OH \cdot C_{10}H_6Ac$, crystallises in colourless prisms, m. p. 198°, and forms an *oxime*, m. p. 164°, and a *phenylhydrazone*, m. p. 133°. 2 : 4-*Diacetyl-α-naphthol* forms long, slender, colourless needles, m. p. 140°, and is more soluble in toluene than the above compound. It yields the 2-*mono-oxime*, m. p. 212°, and a *dioxime*, m. p. 220°.

In the β-naphthol series, Gattermann had prepared acetyl-β-naphthyl methyl and ethyl ethers. The authors have now condensed β-naphthyl methyl ether ("nerolin") with acetyl chloride by the Friedel-Craft's process in benzene. Following the above plan, the sodium carbonate extract yielded an acetyl-β-naphthol, m. p. 64—65°, and a diacetyl-β-naphthol, whilst the sodium hydroxide solution contained β-naphthol and the remaining ether Gattermann's acetyl-β-naphthyl methyl

ether, m. p. 57·5—58°, which gave the above acetyl-β-naphthol in 78% yield on hydrolysis with aluminium chloride. The latter yielded phthalic acid on oxidation, formed azo-dyes, and readily condensed with hydrazine to give a methyl-ββ-naphthindazole. The compound is therefore 3-acetyl-β-naphthol. The diacetyl derivative also gave azo-dyes, but oxidised to trimellitic acid. It is, most probably, 3 : 6-di-acetyl-β-naphthol.

3-*Acetyl-β naphthol* [3-*hydroxy-β-naphthyl methyl ketone*] crystallises in colourless leaflets, m. p. 64—65°, and its *potassium* salt in yellow leaflets. When boiled with 90% hydrazine hydrate in glacial acetic acid, it forms a 3-*methyl-ββ-naphthindazole*, $C_{10}H_6<\overset{N}{\underset{CMe}{|}}>NH$, colourless needles, m. p. 217°. 3 : 6-*Diacetyl-β-naphthol* forms short needles, m. p. 165°, and the alkali *salts*, yellow crystals. When boiled for some time with hydrazine, it deposited the insoluble, yellow *compound*, $(\cdot N{:}CMe\cdot C_{10}H_5<\overset{N}{\underset{CMe}{|}}>NH)_2$, which yielded the parent 6-*acetyl*-3-*methyl-ββ-naphthindazole*, $C_{10}H_5Ac<\overset{N}{\underset{CMe}{|}}>NH$, m. p. 175°, on boiling with hydrochloric acid.

β-Naphthol was also heated with zinc chloride, acetic acid and acetic anhydride, but yielded a resin. β-Naphthyl acetate was therefore submitted to the same treatment, at 150—160°, when a 5% yield of 6-*acetyl-β-naphthol* [6-*hydroxy-β-naphthyl methyl ketone*] was isolated from the tarry product. This crystallised in hexagonal prisms, m. p. 171°, and formed a *hydrazone*, m. p. 295°. It yielded trimellitic acid on oxidation, which gave a clue to its constitution. J. C. W.

The Condensation of Aldehydes with β-Diketones. Hugh Ryan and J. M. Dunlea (*Ber.*, 1914, **47**, 2423—2426).—The authors have already described the preparation of unsaturated β-diketones by condensation of the ester of an unsaturated acid with a saturated ketone in the presence of sodium or sodamide (A., 1913, i, 1067). In extension of this work, endeavours have been made to obtain like products by condensing an aldehyde with an alkylated β-diketone in the presence of a dehydrating agent (compare Heller, A., 1914, i, 563).

As benzaldehyde and acetylacetone in the presence of hydrogen chloride undergo condensation as described by Knoevenagel and Werner (A., 1895, i, 48) with formation of a substance $C_{12}H_{13}O_2Cl$, which on elimination of hydrogen chloride yields a substance of the structure $CHPh{:}CAc_2$ (Knoevenagel and Vieth, A., 1895, i, 50), it is necessary to protect the methylene group of the diketone. For this reason dimethylacetylacetone has been made to undergo condensation with benzaldehyde by saturating the mixture at −15° with hydrogen chloride; after four days at 0° there was obtained a *substance*, $C_{25}H_{23}O_2Cl$, colourless prisms, m. p. 170° (decomp.) with previous reddening near 148°; the same substance was also obtained by similar treatment of methylacetylacetone. When the condensation product was boiled with pyridine there was produced a colourless substance, $C_{25}H_{22}O_2$, m. p. 168—169°, probably 2:5-*diphenyl*-4-*benzylidene*-3-*methyl*-

tetrahydropyrone, $CO<^{CHMe\text{---}CHPh}_{C(:CHPh)\cdot CHPh}>O$; this gives a *dibromide*, which decomposes on heating, and a *hydroxylamine* derivative, $C_{25}H_{23}O_2\cdot NH\cdot OH$, needles, m. p. 189—190°. The formation of the pyrone compound is explained by the stages $CMe_2Ac_2 + C_6H_5\cdot CHO \longrightarrow CHPh{:}CH\cdot CO\cdot CMe_2Ac \longrightarrow CHPh{:}CH\cdot CO\cdot CHMeAc \longrightarrow$

$$CHPh{:}CH\cdot CO\cdot CH_2Me \xrightarrow{C_6H_5\cdot CHO} CHPh{:}CH\cdot CO\cdot CHMe\cdot CHPh\cdot OH \longrightarrow CO<^{CHMe\cdot CHPh}_{CH_2\text{---}CHPh}>O \xrightarrow{C_6H_5\cdot CHO} CO<^{CHMe\text{---}CHPh}_{C(:CHPh)\cdot CHPh}>O.$$

D. F. T.

*iso*Curcumin. II. Gustav Heller (*Ber.*, 1914, **47**, 2998—3000. Compare A., 1914, i, 563).—Ryan and Dunlea (preceding abstract) found that benzaldehyde condenses with mono- or di-methylacetylacetone under the influence of hydrogen chloride to give a colourless, chloro-derivative, and therefore criticised the author's interpretation of the condensation in the case of vanillin. This criticism is unjustified, for *iso*curcumin, the product of the condensation of vanillin and acetylacetone, is a chlorine-free dye.

*iso*Curcumin only shows a faint reaction with ferric chloride and is therefore regarded as a mixture of ketones with a little enol, whereas curcumin is decidedly enolic. The *ethylcarbonato*-derivatives have been prepared by shaking cold, alkaline solutions with ethyl chlorocarbonate; the compound with the natural curcumin forms yellow leaflets, m. p. 151 - 152°; the *iso*curcumin compound has m. p. 142°. Dihydrocurcumin, $C_{21}H_{24}O_6$, has been obtained in colourless, hard crystals, m. p. 95—96°, by catalytic reduction, but *iso*curcumin remained unchanged under similar conditions.

J. C. W.

Chlorinations with Aqua Regia. Preparation of Chloranil and Bromanil from Phenol. Richard Kempf and Hans Moehrke (*Ber*, 1914, **47**, 2615—2622. Compare Gluud and Kempf, T., 1913, **103**, 1530; Datta, A., 1914, i, 701; Datta and Fernandes, A., 1914, i, 675).—A summary of the author's earlier work on the subject.

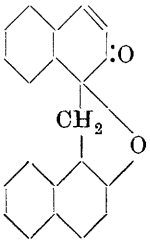
Chloranil can be prepared very conveniently by the action of aqua regia on phenol; the product is very pure and is obtained in 60% yield, or if iodine is present as catalyst, in 76% yield. Chloro- and nitro-phenols give the same product.

By treating phenol with a mixture of concentrated hydrobromic and nitric acids, bromanil can be obtained, but endeavours to prepare iodoanil by the action of iodine and nitric acid were fruitless, 6-iodo-2 : 4-dinitrophenol, however, being isolable from the reaction product.

D. F. T.

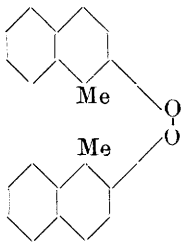
Oxidation of Phenols. II. Dehydromethylnaphthol, a Contribution to the Knowledge of Aroxyls and Methylenequinones. Rudolf Pummerer and Emil Cherbuliez (*Ber.*, 1914, **47**, 2957—2973. Compare A., 1914, i, 714).—The remarkably active substances described in the first paper were derived from a complicated compound, di-β-naphthol. It is now found that the much simpler

1-methyl-β-naphthol also yields a dehydro-compound which is analogous to hydroxydinaphthylene oxide.

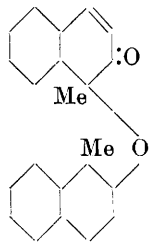


Abel (A., 1893, i, 172) described an oxidation product of di-β-naphtholmethane which he regarded as a peroxide. The same compound is obtained in sulphur-yellow leaflets, m. p. 171—172°, by the oxidation of the dinaphtholmethane with alkaline ferricyanide. It is easily reduced again, it does not oxidise quinol or react with triphenylmethyl, but it is sensitive towards permanganate and forms only a *monophenylhydrazone*, orange needles, m. p. 168—169°. Consequently, it is not a peroxide at all, but should be regarded as the *quinol ether* form of *dehydrodinaphtholmethane*, annexed formula.

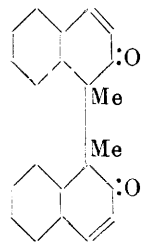
1-Methyl-β-naphthol (Fries and Hübner, A., 1906, i, 190) is oxidised by alkaline ferricyanide or ferric chloride to the same compound, pale yellow prisms, m. p. 133—134°, as Fries and Hübner obtained by the action of nitrous acid. The combustion, titration with stannous chloride, and molecular-weight determination point to the fact that the substance is a bimolecular compound and certainly not 1 : 2-naphthamethylenequinone as originally stated. As in the case of hydroxydinaphthylene oxide, there remain three possible formulæ for this *dehydro-1-methyl-β-naphthol*:



I.

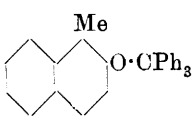


II.



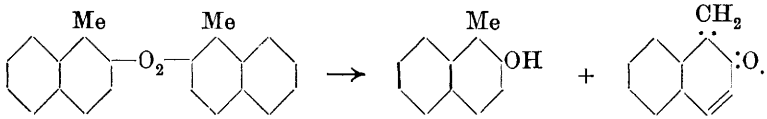
III.

The fact that the compound reacts almost quantitatively with triphenylmethyl in boiling benzene to form *triphenylmethyl 1-methyl-β-naphthyl ether*, annexed formula, colourless tablets, m. p. 151—152°, without the separation of methylnaphthol as a by-product, supports the peroxide formula I. The constitution of this ether is shown by its scission into 1-methyl-β-naphthol and triphenylcarbinol by alcoholic hydrogen chloride, by its reduction to triphenylmethane and methylnaphthol in alcoholic sulphuric acid, and by its indifference towards bromine, permanganate or phenylhydrazine. That the above dehydro-1-methyl-β-naphthol does behave as a peroxide is further shown by its oxidation of quinol to quinone, liberation of iodine from potassium iodide, and indifference towards bromine, phenylhydrazine or oxygen.



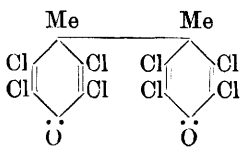
The competitive formulæ, II and III, would seem to be superfluous but for the possibility of the compound dissociating into radicles in indifferent media. The above reaction with triphenylmethyl would be explained by the intervention of an aroxyl radicle with univalent

oxygen, but the existence of this cannot be proved by molecular-weight determinations or optical methods. There is only one slight piece of evidence in favour of an α-ketomethyl radicle, namely, that the compound is sensitive towards permanganate. At any rate, it seems that the aroxyl form is favoured in this case, whereas the reactions of hydroxydinaphthylene oxide pointed to the α-ketomethyl form. The dehydromethylnaphthol liberates the violet α-ketomethyl radicle from warm benzene solutions of hydroxydinaphthylene oxide, but an excess causes the colour to become pale again. The decomposition of dehydromethylnaphthol in boiling xylene or glacial acetic acid leads to the formation of 1-methyl-β-naphthol and, apparently, a polymeride of naphthamethylenequinone, according to the scheme:



The methylenequinone which Fries and Hübner obtained from 6-bromo-1-methyl-β-naphthol can also be prepared by oxidation with one equivalent of potassium ferricyanide. The product is now shown to be a *dehydro*-6-*bromo*-1-*methyl*-β-*naphthol*, in analogy with the above. It is found to exist in two forms, long, yellow prisms, m. p. 119—120°, and yellow leaflets, m. p. 144°.

Similarly, Zincke's tetrachloro-*p*-methylenebenzoquinone (A., 1903, i, 757) has been obtained from tetrachloro-*p*-cresol and shown to be in reality, *dehydrotetrachloro*-p-*cresol*, annexed formula, for its power to oxidise quinol is only half that required by Zincke's formula.



The importance of the aroxyl and the isomeric α-ketomethyl radicles as intermediaries in the oxidation of phenols is emphasised.

J. C. W.

Preparation of Nitroaminoanthraquinones. Badische Anilin- und Soda Fabrik (D.R.-P. 279866; from *J. Soc. Chem. Ind.*, 1915, **34**, 347).—The formaldehyde compounds of α-aminoanthraquinones, or the free bases mixed with formaldehyde or with substances capable of yielding it, are nitrated. The *o*- or *p*-nitroaminoanthraquinones are obtained in the free state or as their formaldehyde compounds, which are readily hydrolysed by boiling with dilute alkali. J. C. W.

Preparation of Anthraquinone Derivatives Containing Sulphur. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 277439; from *J. Soc. Chem. Ind.*, 1915, **34**, 270).—Anthraquinonyl mercaptans or disulphides are treated with halogens in the absence of water. The products may be used for the preparation of dyes. They form ester-like compounds with alcohols, which yield sulphenic acids containing the group –S·OH, on hydrolysis. With phenols, they form hydroxyarylanthraquinonyl sulphides, and they condense with aromatic hydrocarbons under the influence of aluminium chloride, yielding arylanthraquinonyl sulphides. J. C. W.

Methylanthracene from Frangula-Emodin. N. KRASOVSKI (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1067—1075).—By the reduction of catharto-emodin by means of hydrogen and zinc dust the author (A., 1909, ii, 174) obtained a methylanthracene similar in all its properties to that obtained by Fischer (A., 1875, 1021) and Liebermann (A., 1877, i, 610), and described by them as 2-methylanthracene. The methylanthracene obtained from frangula-emodin is, however, regarded by Perkin and Hummel (T., 1894, **65**, 925), Hesse (A., 1900, i, 40), and Jowett and Potter (T., 1903, **83**, 1327) as 1-methylanthracene, but Oesterle and Tisza (A., 1908, i, 905) and Fischer, Gross, and Neber (A., 1911, i, 886) consider it to be the 2-derivative.

The author has prepared synthetically 1- and 2-methylanthracenes and several of their derivatives, the melting points being compared with those of the corresponding compounds obtained from frangula-emodin. The conclusion is drawn that the latter yields 2-methylanthracene.

On further purification, the methylanthracene from catharto-emodin, and the methylanthraquinone and anthraquinonecarboxylic acid prepared from it, are found to have melting points identical with those of the 2-methylanthracene derivatives. T. H. P.

1 : 4 : 9 : 10-Anthradiquinone. R. LESSER (*Ber.*, 1914, **47**, 2526—2528).—By oxidation of quinizarin in hot benzene solution with lead dioxide, 1 : 4 : 9 : 10-*anthradiquinone* has been obtained. This substance, which forms brownish-red needles, m. p. indistinct near 185°, exhibits the character of a true quinone and in this resembles 1 : 4-anthraquinone (Dienel, A., 1906, i, 290); the other known anthraquinones, namely, the 9 : 10 and 1 : 2, appear not to be typical quinones. 1 : 4 : 9 : 10-Anthradiquinone can be sublimed at 160°; its solutions show a yellowish-red to brownish-red colour, and a stronger fluorescence than that given by quinizarin. It possesses the usual chemical reactions of a quinone, but attempts to prepare a quinhydrone compound were unsuccessful. D. F. T.

Menthol. Its Melting and Solidifying Points. ROBERT MELDRUM (*Chem. News*, 1915, **111**, 229—231).—An investigation of the melting and solidifying points of "ordinary pure" menthol under various conditions. As is to be expected, the temperature of solidification is less definite than the m. p., and not only varies with different methods, but may also show a range of several degrees in determinations by one method. The melting point is constant at 42°. Experiments were also made with menthol containing 2% of water and 20% of oil of peppermint, the m. p. of these mixtures being 35° and 34·5° respectively. D. F. T.

Menthol and Certain of its Derivatives. N. I. KURSANOV (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 815—845).—When the constant menthyl chloride previously described (A., 1901, i, 553) is subjected to Grignard's reaction, it yields: (1) menthene; (2) menthane; (3) a crystalline dimenthyl, $(C_{10}H_{19})_2$, m. p. 105—106°, $[\alpha]_D$ −51·42°, identical with that obtained by the action of sodium on the same menthyl chloride, and (4) natural *l*-menthol, no isomeride of the latter being formed. With ordinary menthyl chloride, the same reaction

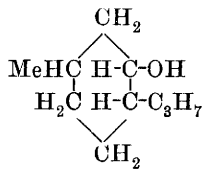
gives, in addition to the above products, a liquid dimenthyl and a liquid menthol. The conclusion is drawn that the constant menthyl chloride is, both structurally and as regards the spacial arrangement of its atoms, analogous to natural, crystalline *l*-menthol.

Menthanecarboxylic acid, $CHMe\langle\begin{matrix}CH_2\cdot CH(CO_2H)\\CH_2\text{———}CH_2\end{matrix}\rangle CHPr^{\beta}$, obtained by the action of carbon dioxide on the organo-magnesium compound corresponding with the constant menthyl chloride, forms flat needles or large, rectangular plates, m. p. 65—66°, $[\alpha]_D$ −54·16°. From ordinary menthyl chloride, this acid is obtained together with a smaller proportion of a liquid acid, the latter being formed from the "inconstant" menthyl chloride.

The chloride obtained by the action of phosphorus pentachloride on menthol consists of a mixture of at least two stereoisomeric secondary chlorides, $CHMe\langle\begin{matrix}CH_2\cdot CHCl\\CH_2—CH_2\end{matrix}\rangle CHPr^{\beta}$ (I) and

$$CHMe\langle\begin{matrix}CHCl\cdot CH_2\\CH_2—CH_2\end{matrix}\rangle CHPr_{\beta}\ (II),$$

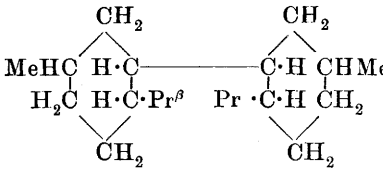
with rotations of opposite sign, and possibly contains also the tertiary chloride, $CHMe\langle\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\rangle CPr^{\beta}Cl$, which may be formed from (I) by loss and subsequent addition of hydrogen chloride. Menthol and the chlorides corresponding structurally with it contain three asymmetric carbon atoms, four pairs of optical antipodes and four racemic mixtures being possible. The action of phosphorus pentachloride on menthol is accompanied by rearrangement of the substituent groups, a mixture of stereoisomeric menthyl chlorides being formed. Two of the four possible chlorides would have the chlorine and the neighbouring tertiary hydrogen distant one from the other and would be stable, the other two, in which the chlorine and hydrogen are adjacent, being unstable. The author's investigations, as yet incomplete, on the menthanecarboxylic acids formed from ordinary menthyl chloride by the Grignard reaction, indicate the formation of only two such acids, one liquid and the other crystalline. Consequently, ordinary menthyl chloride contains only two secondary stereoisomerides, one stable and one unstable. The formation of these two chlorides is readily explained on the supposition that the spacial rearrangement occurring during the action of phosphorus pentachloride on menthol affects only the groups of the carbon atom to which the hydroxyl is attached, this being the carbon atom taking immediate part in the reaction. In the stable menthyl chloride, the chlorine and the adjacent tertiary hydrogen atoms occupy anti-positions, and since this chloride is converted by the Grignard reaction into natural *l*-menthol, the latter will have the annexed structure.



l-Menthone, which corresponds in spacial structure with ordinary *l*-menthol, undergoes partial inversion into the strongly dextro-rotatory *iso*menthone when treated with sulphuric acid (compare Beckmann, A., 1909, i, 245). According to Beckmann (A., 1897, i, 248), the asymmetric carbon atom concerned in this inversion is the one

to which the *iso*propyl radicle is united, the original lævo-rotation of this carbon atom being changed to a dextro-rotation in *d-iso*menthone. Since the rotation of the latter is considerably greater than that of *l*-menthone, the rotation due to the asymmetric carbon united with the menthyl group must be positive in sign. On the assumption that *l*-menthone corresponds with natural *l*-menthol and not with the stereoisomeride in which the hydrogen and hydroxyl of the hydroxylic carbon atom are interchanged, it follows that the carbon atom connected with the *iso*propyl group of *l*-menthol produces a lævo-, and that connected with the menthyl group a dextro-rotation.

The spacial structure of menthanecarboxylic acid, m. p. 65—66°, is determined by that of the constant menthyl chloride, the carboxyl and the *iso*propyl group occupying *syn*-positions. As regards the liquid menthol and the liquid menthanecarboxylic acid obtained with the crystalline menthol and the crystalline acid from crude menthyl chloride, these are formed from the unstable *syn*-chloride, the hydroxyl (or carboxyl) group probably occupying the *anti*-position to the *iso*propyl group. Ethylmenthane (A., 1901, i, 553) should correspond in structure with constant menthyl chloride, the ethyl and *iso*propyl groups being in *syn*-positions. The crystalline dimenthyl, being obtained from constant menthyl chloride, has the annexed structure.



When the potassium or sodium derivative of menthol is heated with iodo- or bromo-benzene, benzene and menthone are formed, but in presence of finely-divided copper (Naturkupfer) (compare Ullmann and Sponagel, A., 1905, i, 644; 1907, i, 38) the reaction yields, besides these products, *phenyl menthyl ether*, $C_{10}H_{19}\cdot OPh$, which crystallises in flat needles with a slight aromatic odour, m. p. 52—53°, b. p. 150—151°/12 mm., $[\alpha]_D$ in benzene solution —128·11°, and has the phenyloxy- and the *iso*propyl groups in *syn*-positions. For the preparation of ethers by Ullmann and Sponagel's reaction it is, therefore, not necessary that both radicles shall be aromatic, and the author has prepared phenetole in 35—45% yield from iodobenzene and sodium or potassium ethoxide in presence of copper. When the latter is absent, the whole of the iodobenzene is converted into benzene, and no acetaldehyde, although this would be expected, is formed; the ability of alkyloxides to reduce aromatic halogenated derivatives has been previously observed by Balbiano (A., 1882, 168) and by Blau (A., 1887, 242), but it is uncertain whether the reactions studied by Löwenherz (A., 1900, ii, 338) were really reductions.

When phenyl menthyl ether is heated with fuming hydrochloric acid in a sealed tube at 170°, it yields phenol, the unstable menthyl chloride and *menthylphenol*, $C_{10}H_{19}\cdot C_6H_4\cdot OH$, which is a colourless, immobile, optically inactive resin, b. p. 179—186°/11 mm., solidifying in snow to a vitreous mass, and yielding the inactive *phenylurethane*, $NHPh\cdot CO_2\cdot C_{16}H_{23}$, in small scales, m. p. 141°, together with a small proportion of a compound, m. p. 136°, when treated with phenylcarbimide. When menthylphenol is heated with hydrochloric acid, it

is partly converted into phenol and menthyl chloride, the change proceeding until a condition of equilibrium is attained. T. H. P.

Terpenes and Ethereal Oils. CXVII. Isomerism in the Thujamenthone Series. O. WALLACH (*Annalen*, 1915, **408**, 163—182).—A more careful examination has shown that the thujamenthone (now called β-thujamenthone) obtained by reducing *iso*thujone by the Paal-Skita method (A., 1911, i, 469) is isomeric, not identical as stated, with the thujamenthone (α-thujamenthone) obtained by the reduction of *iso*thujone by sodium and alcohol and subsequens oxidation of the thujamenthol. The two isomerides are regarded at being chemically, not merely physically, isomeric, because their b. p.'s are different. The purest α-thujamenthoneoxime obtainable crystallises in large, transparent prisms, m. p. 97°; the semicarbazone has m. p. 185°. α-Thujamenthone, regenerated from the latter, has b. p. 209—209·5°, D^{18} 0·8915, and n_D 1·4474, and yields by reduction with sodium and alcohol α-thujamenthol, b. p. 212—214°, D^{19} 0·8990, and n_D 1·4611.

[With WALTHER LOHSE.]—α-Thujamenthylamine, obtained by the reduction of the pure oxime, has b. p. 196—197°, and forms a hydrochloride, m. p. 187°, acetyl derivative, m. p. 129—130°, benzoyl derivative, m. p. 106—107°, carbamide, m. p. 205°, phenylcarbamide, m. p. 111—112°, and trimethylammonium iodide, m. p. 199—200°. It reacts with nitrous acid to form α-thujamenthol and hydrocarbons.

β-Thujamenthone, obtained from *iso*thujone by the Skita method or, in the form of the oxime by the reduction of *iso*thujoneoxime, m. p. 119—120°, by the hydrogen-palladous chloride-gum arabic method, is purified through the *oxime*, m. p. 130—131°, and the *semicarbazone*, m. p. 190—191°, and then has b. p. 215—216·5°, D^{19} 0·8990, and n_D 1·4511. It is very difficult to obtain *iso*thujone free from carvotanacetone, and to this cause is attributed the error mentioned above.

By warming with glacial acetic and sulphuric acids, β-thujamenthoneoxime is converted into an iso-*oxime*, $C_{10}H_{19}ON$, m. p. 102°, which is oxidised by 1% potassium permanganate to a *hydroxy*iso-*oxime*, $C_{10}H_{19}O_2N$, m. p. 148—149°.

In the reduction of *iso*thujoneoxime mentioned above a by-product is a *base* (*iso*thujylamine ?), b. p. 207°, which forms a *benzoyl* derivative, m. p. 147—148°, *carbamide*, m. p. 160°, *phenylcarbamide*, m. p. 167—168°, and *phenylthiocarbamide*, m. p. 151—152°.

β-Thujamenthol, obtained by reducing β-thujamenthone with sodium and alcohol, has b. p. 216·5—217·5°, D^{19} 0·8995, and n_D 1·4583, and yields by heating with zinc chloride at 190° a *thujamenthene*, $C_{10}H_{18}$, b. p. 161—164°, $D^{18\cdot5}$ 0·8100, and n_D 1·4514, whereas the thujamenthene obtained from α-thujamenthol under the same conditions has b. p. 163—165°, D^{22} 0 8085, and n_D 1·4503; neither of them forms a solid nitrosochloride.

[With WALTHER LOHSE.]—β-Thujamenthylamine, prepared from β-thujamenthoneoxime, has b. p. 206·5°, D^{19} 0·8550, and n_D 1·4571, forms a *hydrochloride*, m. p. above 230°, *acetyl* derivative, m. p. 96° when recently crystallised from methyl alcohol and 115—116° after being dried at a higher temperature, *benzoyl* derivative, m. p. 112°,

carbamide, m. p. 214°, *phenylcarbamide*, m. p. 165°, *phenylthiocarbamide*, m. p. 183°, and *trimethylammonium iodide*, m. p. 230°, is not oxidised to β-thujamenthone by chromic acid, but forms a stable *chromate*, and reacts with nitrous acid to form a *tertiary thujamenthol*, $C_{10}H_{20}O$, m. p. 93°, b. p. 204°. The tertiary alcohol is converted by dilute sulphuric acid at 110° into a *thujamenthene*, $C_{10}H_{18}$, b. p. 164—166°, D^{21} 0·8100, n_D 1·4466, which forms a *nitrosochloride*, m. p. 108°; the latter very readily loses hydrogen chloride, yielding *iso*thujone-oxime.

Although it is thus possible to convert β-thujamenthone into *iso*-thujone and vice versa, attempts to convert a member of the α-thuja-menthone series into one of the β-series, or vice versa, have been unsuccessful.

The oxidation of β-thujamenthone by potassium permanganate yields a ketonic *acid* (*semicarbazone*, m. p. 201°), which is converted by sodium hypobromite into the same dicarboxylic acid, $C_9H_{16}O_4$, m. p. 137—138°, as is obtained from α-thujamenthone by the same series of reactions.

During the experiments on the oxidation of β-thujamenthone it was discovered that the crude ketone, obtained from *iso*thujone by Skita's method, contained an appreciable amount of tetrahydrocarvone, which was isolated in the form of the oxime. C. S.

Isomeric Linalools and the Scission of Inactive Linalool into the Optical Antipodes. V. Paolini and Laura Divizia (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 171—176).—The authors describe a method for the preparation of pure linalool. The linalool is converted into the hydrogen phthalate as follows: the alcohol is treated with an excess of sodium in 2—3 volumes of light petroleum; the sodium salt is converted into phthalate, and this is precipitated as hydrogen phthalate on acidification. A concentrated alcoholic solution of the phthalate is treated with the calculated quantity of strychnine, and the *strychnine* salt, $C_6H_4(CO_2{\cdot}C_{10}H_{17})(CO_2H,C_{21}H_{22}O_2N_2)$, is crystallised. Samples of dextro- and of lævo-rotatory linalool from various sources all gave a strychnine salt of m. p. 143—144° (previously softening), and on saponification the strychnine salts all yielded linalool of b. p. 197—198°, D 0·869, n_D 0·870.

Synthetic linalool prepared from geraniol is practically inactive. By recrystallisation of the strychnine salt the authors have isolated the optical antipodes. The less soluble strychnine salt has m. p. 155—156°, and yields on saponification *d*-linalool, $[\alpha]_D$ +1·70°, whilst from the salt in the mother-liquor *l*-linalool of $[\alpha]_D$ −1·60° was obtained. R. V. S.

α- and β Santalols. V. Paolini and Laura Divizia (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 226—230).—If the mixture of α- and β-santalols which occurs in commerce is carefully fractionated, a partial separation of the two isomerides can be effected. If then each of these is converted into the hydrogen phthalate, and this again into the strychnine salt (compare preceding abstract), recrystallisation of the

strychnine salt can be continued until m. p. and rotatory power are constant. When this point is reached, saponification yields the pure isomeride. This can be confirmed by reconverting into strychnine phthalate, which is found to be identical with the original phthalate and to yield a santalol of identical properties when again saponified.

The *strychnine phthalate* of *β-santalol*,

$$C_6H_4(CO_2\cdot C_{15}H_{23})(CO_2H,C_{21}H_{22}O_2N_2),$$

has $[\alpha]_D$ −30·43°, m. p. 134—135°, and the β-santalol obtained from it has b. p. 168—169°/10 mm., D^{15} 0·9729, n_D^{19} 1·5092, $[\alpha]_D$ −42·00°.

The *strychnine phthalate* of *α-santalol* has m. p. 155°, $[\alpha]_D$ −1·40°. The α-santalol prepared fromit has b. p. 159°/10 mm., D^{15} 0·979, n_D^{19} 1·499, $[\alpha]_D$ +1·10°. R. V. S.

Hexahydro-ψ-ionone and Some Derivatives. N. Ishizaka (*Ber.*, 1914, **47**, 2453—2456).—Reduction of geraniol by platinum black and hydrogen gives a mixture of a saturated hydrocarbon, $C_{10}H_{22}$, with a saturated alcohol, $C_{10}H_{22}O$ (Willstätter and Mayer, A., 1908, i, 383); the use of palladium chloride, as in Skita's method, produces a similar result. On using palladium black and hydrogen as recommended by Paal, it is found that reduction in methyl-alcoholic solution occurs only at the ethylenic linkings forming *tetrahydrogeraniol*, $C_{10}H_{21}\cdot OH$, b. p. 212—213°, which could be converted by phosphorus haloids in light petroleum into the *chloride*, $C_{10}H_{21}Cl$, b. p. 85—86°/10 mm., the *bromide*, b. p. 104—105°/14 mm., and the *iodide*, b. p. 126—127°/20 mm.; of these haloids only the bromide was obtained in good yield. Treatment of the bromide in alcoholic solution with ethyl sodioacetoacetate yielded *ethyl tetrahydrogeranylacetoacetate* (*ethyl α-acetyl-δθ-dimethyl*-n-*decoate*), $C_{10}H_{21}\cdot CHAc\cdot CO_2Et$, b. p. 164—166°/10 mm., which gives an intense violet coloration with ferric chloride solution. By hydrolysis with alcoholic potassium hydroxide, the ester was converted into the corresponding ketone, *hexahydro-ψ-ionone* (*methyl δθ-dimethyl*-n-*nonyl ketone*),

$$CH_3\cdot CO\cdot CH_2\cdot C_{10}H_{21},$$

b. p. 119—120°/10 mm., which unlike tetrahydrogeraniol and the corresponding dimethyloctane does not possess characteristic odour; *semicarbazone*, m. p. 95—96°; *oxime*, a pale yellow, viscous oil which is reducible by sodium and alcohol to the corresponding *amine*, $CH_3\cdot CH(NH_2)\cdot CH_2\cdot C_{10}H_{21}$ (*β-amino-ζκ-dimethyl*-n-*undecane*); this is a strong base and forms a *platinichloride*, which when heated decomposes without melting. D. F. T.

Isomerisation Product of Carvone in the Light. Carvonecamphor. E. Sernagiotto (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 70—75).—The paper deals with the constitution of the substance (carvonecamphor) obtained by Ciamician and Silber (A., 1908, i, 555) on exposing an aqueous-alcoholic solution of carvone to the light. Oxidation with permanganate yields a dibasic *acid*, $C_{10}H_{14}O_4$, m. p. 174°, which forms a *silver* salt, $C_{10}H_{12}O_4Ag_2$, crystallising in the disphenoidal class of the rhombic system ($a:b:c=0·5697:1:0·9030$). At the same time a monobasic ketonic *acid*, $C_9H_{12}O_3$, can be isolated; it can

also be formed by the oxidation of the preceding acid with permanganate. The ketonic acid gives a *phenylhydrazone*, $C_{15}H_{18}O_2N_2$, which forms lustrous plates, m. p. 176°, as well as an *oxime*, $C_9H_{13}O_3N$, crystallising in needles, m. p. 167°.

When carvonecamphor is kept with a mixture of alcohol and sulphuric acid for two weeks, an oil is obtained, b. p. 222—224°, which has the formula $C_{10}H_{14}O$, and is termed iso*carvonecamphor*. It yields an *oxime*, $C_{10}H_{15}ON$, m. p. 167°, and a *semicarbazone* $C_{10}H_{14}{:}N_2H{\cdot}CO{\cdot}NH_2$ (needles, m. p. 209°). On oxidation with permanganate, *iso*carvonecamphor yields lævulic acid. On reduction in presence of palladium black a *dihydro*-derivative, $C_{10}H_{16}O$, b. p. 224°, is formed. The dihydro-compound gives an oxime which is liquid, and from which a *benzoyl* derivative, $C_{17}H_{21}O_2N$, m. p. 133°, can be prepared. The dihydro-compound yields lævulic acid on oxidation with warm permanganate.

On reducing carvonecamphor with sodium and alcohol, the corresponding alcohol ("carvoneborneol"), $C_{10}H_{16}O$, b. p. 214°, m. p. 135°, is obtained. On oxidation this gives carvonecamphor again.

R. V. S.

Use of Aqueous Mercuric Acetate in the Analysis of the Terpenic Portion of Essential Oils. L. Balbiano (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 165—171. Compare A., 1906, i, 186).—The oxidising action of aqueous mercuric acetate is greatly accelerated by the action of heat, even where, as with camphene, the terpene forms a mercuriacetate. Mercuric acetate reacts with neither aromatic hydrocarbons (*loc. cit.*), nor *cyclo*paraffins (compare Balbiano and Angeloni, A., 1914, i, 860), nor dicyclic hydrocarbons, $C_{10}H_{18}$, of the pinane type (compare Tausz, *Diss. Karlsruhe*, 1911). Camphene reacts quantitatively with mercuric acetate, being converted into a hydroxycamphene mercuriacetate, which yields 70—94% of the camphene taken on decomposition with zinc and hydrochloric acid; the deficit is due to the difficulty of condensing small amounts of camphene after distillation in a current of steam. Cold aqueous mercuric acetate serves to separate the terpenes from a mixture containing them in conjunction with cyclic, aromatic and paraffinoid hydrocarbons.

T. H. P.

The Autoxidation of Limonene. A. Blumann and O. Zeitschel (*Ber.*, 1914, **47**, 2623—2628).—Only with a few terpenes has the phenomenon of autoxidation been investigated (Blumann and Zeitschel, A., 1914, i, 495; Wallach, A., 1906, i, 194). As limonene is so widespread in nature its examination has now been effected. When purified limonene, D^{15} 0·845, α_{100} + 106°, is exposed to the air in the presence of water in a loosely closed vessel for two and a-half months, crystals of a *substance*, m. p. near 60°, form on the walls above the surface of the liquid and a resinous layer of unknown nature is deposited at the bottom of the liquid. Amongst the products which are volatile in steam, were identified carvone and carveol, both optically inactive. The latter has not previously been obtained in a pure condition, the

purification in this case being effected by successive conversion into the benzoate, hydrolysis, conversion into the phenylurethane, and final hydrolysis. The mother liquors of the phenylurethane yielded a small quantity of an unidentified active alcohol.

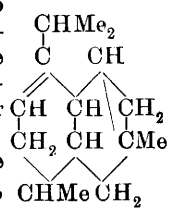
The following derivatives of carveol,

$$CH_2{:}CMe{\cdot}CH\begin{matrix}<CH_2{\cdot}CH(OH)\\ CH_2\text{——}CH>\end{matrix}CMe,$$

D^{15} 0·9578, b. p. 108—110°/11 mm., 226—227°/751 mm., n_D^{18} 1·4961, were prepared; *phenylurethane*, needles, m. p. 94—95°; *acetate*, b. p. 115—116°/10 mm., D^{15} 0·9755; *phthalate*, crystals, m. p. 136—137°; bromine additive *compound*, oily; *benzoate*. On oxidation carveol was converted into carvone and on dehydration by heating with zinc chloride or diluted sulphuric acid gave *p*-cymene. When shaken with 5% sulphuric acid for seventeen hours it underwent hydration to a *substance*, $C_{10}H_{18}O_2$, needles, m. p. 132—133°. D. F. T.

The Constituents of Ethereal Oils. A New Class of Tricyclic Sesquiterpenes: Copaene, $C_{15}H_{24}$. F. W. Semmler and H. Stenzel (*Ber.*, 1914, **47**, 2555—2561).—The ethereal oil obtainable from African copaiba balsam is known to contain in addition to β-caryophyllene and a dextro-rotatory sesquiterpene (di-hydrochloride, m. p. 117—118°, gives *l*-cadinene on elimination of hydrogen chloride; von Soden, A., 1909, i, 401), a second sesquiterpene very similar in chemical properties to the former.

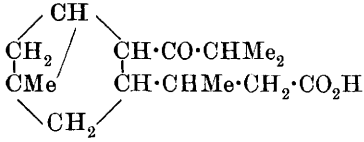
The latter sesquiterpene, now termed *copaene*, was separated by fractional distillation as an oil, b. p. 119—120°/10 mm., D^{15} 0·9077, $[\alpha]_D$ —13·35°, n_D 1·48943, which gives no solid nitrosochloride or nitrosite, but a hydrochloride, m. p. 117—118°, identical with cadinene hydrochloride; the hydrochloride on removal of hydrogen chloride yielded cadinene. The sesquiterpene is therefore in all probability an olefinic tricyclic compound. Reduction of copaene in ethereal solution by hydrogen and platinum produced a *dihydrocopaene*, $C_{15}H_{26}$, b. p. 118—121°/12 mm., *n* 1·47987, D^{18} 0·8926 $[\alpha]_D$ −12·2°, which is therefore also probably tricyclic. The close relationship of copaene with cadinene, which belongs to the hydrogenated naphthalene group, renders it highly probable that the former is of allied structure and the constitution (annexed formula) is provisionally suggested for copaene.



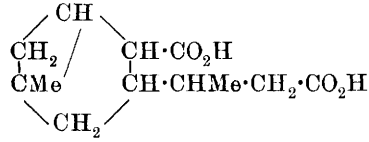
Oxidation of copaene in acetic acid solution by ozone gave rise to a viscid acid substance, *copaeneketonic acid*, $C_{13}H_{23}{\cdot}CO{\cdot}CO_2H$, b. p. 215—225°/17 mm.; this was converted through the colourless *silver* salt into the *methyl* ester, b. p. 177—182°/14 mm., D^{22} 1·0243, n_D 1·47694, $[\alpha]_D$ +29·4°. In the oxidation of copaene by potassium permanganate, a *glycol*, $C_{15}H_{26}O_2$, also was obtained, b. p. 178—185°/17 mm., D^{22} 1·039, n_D 1·50266, α_D +13°. The *semicarbazones* of copaeneketonic acid and its methyl ester are solids, m. p. 221° and 193·5—194° respectively.

Further oxidation in alkaline solution by sodium hypobromite converted copaeneketonic acid into *copaenedicarboxylic acid*, $C_{12}H_{18}O_4$; by

means of its *silver* salt this was converted into the *methyl* ester, b. p. 178—182°/17 mm., D^{24} 1·072, n_D 1·47242, $[\alpha]_D$ + 34°. According to these results it would appear that an *iso*propyl group has been destroyed, and the above formula for copaene is suggested on this evidence. The structures of copaeneketonic acid and copaenedicarboxylic acid are provisionally represented by the annexed formulæ I and II respectively.



(I.)



(II.)

D. F. T.

Composition of the Essential Oil of Italian Wormwood. V. Paolini and R. Lomonaco (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 123—129).—The essential oil of *Artemisia absinthium*, L., contains (1) thujone (about 10%) in the form of a mixture of the α- and β-isomerides; (2) thujyl alcohol (about 48%) in the free state and also as acetate, *iso*valerate, and palmitate; the alcohol obtained is a mixture of at least two chemical individuals, δ-thujyl alcohol predominating. In addition to these substances the authors were able to separate phellandrene, cadinene, and a blue oil of undetermined nature.

R. V. S.

The Constituents of Ethereal Oils. A New Oxide in Java Citronella Oil. K. E. Spornitz (*Ber.*, 1914, **47**, 2478—2482).—By fractionation of the less volatile portion of citronella oil the author has obtained a liquid, $C_{20}H_{34}O$, which appears to be an organic oxide, the oxygen being inert towards acetic anhydride and towards sodium. This substance, *dicitronelloxide*, has the properties: b. p. 182—183°/12 mm., D_{20}^{20} 0·9199, n_D 1·49179, α_D −4°; from the fact that sodium and alcohol fail to affect the compound, it is probable that the two ethylenic linkings are not conjugated. Reduction by platinum-black and hydrogen in ethereal or acetic acid solution converts the substance into *tetrahydrodicitronelloxide*, $C_{20}H_{38}O$, b. p. 180—185°/11·5 mm., D_{20}^{20} 0·9001, n_D 1·47457, α_D 0°. The original substance gives a solid *hydrochloride*, $C_{20}H_{35}OCl$, tablets, m. p. 107·5°, from which hydrogen chloride can be again eliminated by alcoholic potassium hydroxide, the product being an isomeride, iso*dicitronelloxide*, $C_{20}H_{34}O$, b. p. 176—180°/11 mm., D_{20}^{20} 0·9518, n_D 1·49692, α_D +1°; this contains an ethylenic linking less, and therefore a ring more, than the parent compound. Reduction of this oxide by platinum and hydrogen could not be effected, and the *dihydro*iso*citronelloxide*, $C_{20}H_{36}O$, m. p. 71°, was obtained by reduction of the above hydrochloride by sodium and hot alcohol. The action of ozone on the acetic acid solution of dicitronelloxide gave as chief product a *substance*, $C_{18}H_{30}O_3$, D^{20} 1·0395, n_D 1·49013, α_D +4°, from which it would appear that the double bonds are situated outside the ring.

The oxide now described is in all probability quite distinct from the

compound obtained from citronellal and oxalic acid by Semmler and Jonas (*Ber.*, 1914, **47**, 2079). D. F. T.

The Constituents of the Ethereal Oils. The Presence of an Acid, $C_{15}H_{22}O_2$, and of two Lactones, $C_{15}H_{22}O_2$ and $C_{15}H_{20}O_2$, in Costus Root Oil. F. W. SEMMLER and J. FELDSTEIN (*Ber.*, 1914, **47**, 2433—2437. Compare this vol., i, 275).—The chemistry of costus root oil, obtained from the roots of *Saussurea Lappa*, Clarke, has been but little examined up to the present. The roots yield approximately 1% of the oil of which the physical constants are b. p. 60—215°/11 mm., D_{16}^{20} 0·9851, n_D 1·51264, α_D +15·4°. By fractional distillation the oil has now been separated into eight portions, from the least volatile of which, b. p. 200—210°/11 mm., there can be isolated a lactone; this substance, costolactone, was purified by conversion through the *silver* salt into the *methyl* ester of the corresponding hydroxy-acid; this ester on distillation under reduced pressure gave pure *costolactone*, $C_{15}H_{20}O_2$, b. p. 205—211°/13 mm., D^{21} 1·0891, n_D 1·53043, α_D +28°.

From the seventh fraction, b. p. 190—200°, there could be separated by sodium carbonate solution, *costic acid*, $C_{15}H_{22}O_2$, which after conversion into its *silver* salt was obtained as an oil, b. p. 200—205°/11 mm., D^{21} 1·0508, n_D 1·51912, α_D +40°; the *methyl* ester has b. p. 170—175°/11 mm., D^{21} 1·0242, n_D 1·51058, α_D +36°. The portion of this fraction which was insoluble in sodium carbonate contained *dihydrocostolactone*, $C_{15}H_{22}O_2$, which, after purification in the form of the *silver* salt of the corresponding hydroxy-acid, had b. p. 210—213°/19 mm., D^{22} 1·0776, n_D 1·52289, α_D +48°: the *methyl* ester of the corresponding hydroxy-acid regenerated the lactone on distillation under reduced pressure.

Costolactone and dihydrocostolactone are remarkably stable and are only partly affected by sodium hydroxide solution in the cold; the corresponding hydroxy-acids are very unstable. The respective molecular refractions show costolactone and costic acid to be diolefinic bicyclic substances, whilst dihydrocostolactone contains but one double linking. The relationship between these lactones is demonstrated by reduction of each with platinum and hydrogen in ethereal solution, yielding the same *tetrahydrocostolactone*, $C_{15}H_{24}O_2$, b. p. 198—202°/13 mm., D^{21} 1·0451, n_D 1·50510, α_D +33°. The connexion between these lactones and the diolefinic bicyclic costic acid is shown by the action of sulphuric acid of 33% concentration converting costic acid into dihydrocostolactone. D. F. T.

Ethereal Oil of Elsholtzia cristata, Willdenow. Y. ASAHINA and Y. MURAYAMA (*Arch. Pharm.*, 1914, **252**, 435—448).—By distillation with steam dried *Elsholtzia cristata* yields about 2% of a mobile, yellow oil, b. p. 210—215°, D^{15} 0·970, acid number 0, saponification number 14·84, and, after acetylation, 14·7, which does not contain an acid, ester, aldehyde, phenol, or a methyl ether, but reacts with semicarbazide and with hydroxylamine to form respectively a *semicarbazide*, $C_{11}H_{17}O_2N_3$, colourless leaflets, m. p. 171°, and an *oxime*, $C_{10}H_{15}O_2N$, colourless prisms, m. p. 54°. The *ketone*, $C_{10}H_{14}O_2$,

regenerated from either of these derivatives, is called *elsholtzione*. It is an almost colourless, mobile liquid having a peculiar, aromatic odour, b. p. 87—88°/10 mm., 112°/31 mm. and 210°/764 mm., D^{20} 0·9817, α_D 0°, and n_D^{21} 1·48424. It does not respond to the pine-shaving test, but in Liebermann's reaction a rose-red to reddish-violet coloration is developed, becoming olive-green by keeping. By reduction with hydrochloric acid and amalgamated zinc, the ketone yields a *substance*, $C_{10}H_{16}O$, b. p. 73—75°/17 mm., which is not a ketone, and yields by heating with alcoholic ammonia at 200° a substance the vapour of which develops an intense violet-red coloration in the pine-shaving reaction.

Elsholtzione yields *iso*valeric acid by oxidation with 5% potassium permanganate, and by treatment in dry ether with sodium and amyl nitrite is converted into an *acid*, $C_6H_6O_3$, colourless needles, m. p. 134°. This acid, which is called *elsholtzic acid*, appears from its behaviour and properties to be homopyromucic acid; if this is so, elsholtzione may be a furan derivative, $C_4OH_2Me\cdot CO\cdot CH_2\cdot CHMe_2$.

The following new compounds have been prepared by the reaction of pyromuconitrile and the magnesium alkyl haloid in the usual manner: *furyl ethyl ketone*, $C_4OH_3\cdot COEt$, colourless crystals, m. p. 28°, b. p. 182—183°, D^{28} 1·0626, n_D^{28} 1·49837 (*semicarbazone*, leaflets, m. p. 188—190°); *furyl* n-*propyl ketone*, b. p. 192°, D^{20} 1·0485, n_D^{20} 1·49165 (*semicarbazone*, prisms, m. p. 190°); *furyl* iso*butyl ketone*, b. p. 207°, D^{19} 1·0110, n_D^{19} 1·48905 (*semicarbazone*, prisms, m. p. 174°); and *furyl* iso*amyl ketone*, b. p. 221°, D^{22} 0·9900, n_D^{23} 1·48315 (*semicarbazone*, needles, m. p. 101°).

These ketones do not give a green coloration in the pine-shaving reaction, are converted into pyromucic acid by sodium and amyl nitrite, and exhibit more or less intense colour reactions similar to those of elsholtzione; the last two ketones also resemble elsholtzione in their odour. C. S.

Resin of Picea Vulgaris, L., var. Montana Schur. Hans Binder (*Arch. Pharm.*, 1914, **252**, 547—589).—The resins of *Picea vulgaris*, Transylvanian pine, and Jura turpentine are not identical.

The crude resin of *Picea vulgaris* employed by the author was a mixture of resin, particles of wood, pine-needles, and sand; it had a bitter taste and an intense odour of vanillin (this substance was detected by colour reactions). The examination was conducted along four lines: (1) isolation of crystals from the crude resin by physical and mechanical methods, (2) isolation of crystals from the fused resin by similar methods, (3) isolation of all the constituents of the crude resin by Tschirch's method, and (4) a similar treatment of the fused resin. These courses were adopted in order to prove that a separation of the constituents, by physical and mechanical methods only, is impossible. The crystalline substances obtained by (1) and (2), by the successive operations of solution in cold 70% alcohol, filtration, and fractional crystallisation, are different from those obtained by (3) and (4), and are shown to be mixtures; their m. p., acid, saponification and iodine numbers, and specific rotations are recorded.

The examination of the resin by Tschirch's method gives the follow-

ing results. The ethereal solution of the resin is exhaustively extracted with 1% ammonium carbonate, 1% sodium carbonate, and 1% potassium hydroxide successively; the residue, after removal of volatile matter by distillation with steam, consists of resene. Much better results and more rapid separations are obtained with the fused than with the crude resin. The 1% ammonium carbonate extracts (fifteen repetitions are necessary) contain *α-piceapimaric acid*, $C_{20}H_{30}O_2$, monoclinic crystals, m. p. 164—166°, $[\alpha]_D - 22°5'$ in alcohol ($c = 4·656$), acid number 189·70 (direct method) and 193·07 (indirect), saponification number variable, iodine number 81·4, which forms a *silver* and a *lead* salt, and exhibits the phytosterol colour reactions. An amorphous *acid*, m. p. 101—116°, $[\alpha]_D - 8°9'$ in alcohol ($c = 1·226$), and an *acid*, m. p. 80—86°, $[\alpha]_D - 14°53'$ ($c = 1·9047$), are also present in the ammonium carbonate extracts.

The 1% sodium carbonate extracts (19 repetitions) contain three isomeric piceapimaric acids, $C_{20}H_{30}O_2$. The *β*-acid is precipitable from its alcoholic solution by lead acetate; it crystallises in monoclinic leaflets, m. p. 156—157°, $[\alpha]_D - 24°44'$ in alcohol ($c = 5·861$), acid number 189·54 (direct) and 175·50 (indirect), iodine number 76·92, and forms a *silver* and a *lead* salt, the latter being insoluble in ether. *γ-Piceapimaric acid*, which is not precipitated from its alcoholic solution by lead acetate, crystallises in leaflets, m. p. 151—153°, $[\alpha]_D - 4°17'$ in alcohol ($c = 4·66$), acid number 186·61 (direct) and 187·77 (indirect), iodine number 83·78, and forms a *silver* salt and a *lead* salt which is insoluble in ether. *δ-Piceapimaric acid*, monoclinic(?) crystals, m. p. 161—162°, $[\alpha]_D - 17°8'$ in alcohol ($c = 2·043$), acid number 191·25 (direct) and 182·35 (indirect), iodine number 87·15, forms a *silver* salt and a *lead* salt which is soluble in alcohol and in ether. All three isomerides exhibit colour reactions with the phytosterol reagents.

The 1% potassium hydroxide extracts do not contain any acidic substances.

Since it is not certain that the rotatory power of a resin acid is the same at different concentrations, the author recommends that the rotations of all resin acids should be measured in alcoholic solution ($c = 5$). C. S.

Oleoresin of Sand Pine. A. W. Schorger (*J. Ind. Eng. Chem.*, 1915, **7**, 321—322).—A specimen of oleoresin obtained from the sand pine (*Pinus clausa*) yielded volatile oil 18·93%, resin 72·30%, water 6·10%, and other substances 2·67%. The volatile oil had D_{15}^{15} 0·8725, n_D^{15} 1·4768, and $\alpha_D^{20} - 22·49°$, and consisted of *l*-*α*-pinene 10%, *l*-camphene 10%, *l*-*β*-pinene 75% (losses by polymerisation, etc., 5%). The resin contained 4% of resene, the remainder consisting chiefly of abietic acid. W. P. S.

Siam Benzoin. Friedrich Reinitzer (*Arch. Pharm.*, 1914, **252**, 341—349).—In 1893 Lüdy stated that Siam benzoin consists essentially of the benzoic esters of two alcohols, benzoresinol and siaresinotannol. The former of these alcohols cannot be benzoylated, and the benzoate of the latter is described by Lüdy as a brown

amorphous substance. Since Siam benzoin always occurs as an opaque, quite colourless substance (coated with a reddish-yellow crust produced by atmospheric oxidation), the author has again examined the substance in order to explain these discrepancies. He finds that it is a mixture of three colourless, crystalline substances, benzoic acid, *siaresinol* (the benzoresinol in Siam benzoin is not identical with the benzoresinol in Sumatra benzoin and is therefore called siaresinol), and *lubanyl benzoate*, which will be described in a subsequent paper.

C. S.

[The Araliaceae Family, etc.] **Reply to Halberkann.** A. W. VAN DER HAAR (*Arch. Pharm*, 1914, **252**, 421—424. Compare A., 1914, i, 122; Halberkann, *ibid.*, 1041).—The author quotes references in the literature to refute Halberkann's criticisms. C. S.

Constitution of Cantharidin. J. GADAMER (*Arch. Pharm.*, 1914, **252**, 609—632).—A theoretical paper in which the author discusses the observations recorded by the numerous investigators of this substance and its derivatives, and arrives at the conclusion that a satisfactory formula cannot yet be ascribed to it. C. S.

Chemical Nature of Cantharidin. P. W. DANCKWORTT (*Arch. Pharm.*, 1914, **252**, 632—636).—The alkali consumed when cantharidin in acetone solution is titrated with *N*/2-potassium hydroxide, phenolphthalein being the indicator, corresponds with the presence of more than one carboxyl group, and indicates, as Spiegel has observed, that cantharidin is an acid anhydride. The potassium salt, $C_{10}H_{12}O_5K_2$, obtained is decomposed by water, but the *brucine* salt, prepared from 1 mol. of cantharidin and 2 mols. of brucine in hot water, is a stable, crystalline substance. Attempts to resolve cantharidin into optical antipodes by means of the brucine salt have been unsuccessful.

C. S.

Action of Hydrogen Haloids on Cantharidin. J. GADAMER (*Arch. Pharm.*, 1914, **252**, 636—663).—The "di-iodide," $C_{10}H_{12}O_3I_2$, obtained by Piccard in 1877 by heating cantharidin with concentrated hydriodic acid, may be of the utmost importance in the elucidation of the constitution of cantharidin provided it can be shown that the reducing function of hydrogen iodide has not come into play. The author, therefore, after repeating the experiment under Piccard's conditions and obtaining the "di-iodide," m. p. 133—137° (Piccard gave 131°), and a mixture of acids which is under investigation, initiated a series of experiments in which the hydriodic acid used was mixed with 10% of iodine in order to repress the dissociation at elevated temperatures, and thus to prevent the reducing action of the acid. Under such conditions, by heating cantharidin with hydriodic acid (D 1·7) at 100° under 1·5 to 1·8 atm., no change is effected, but under 4 to 4·2 atm. about 20% of the cantharidin is converted into cantharic acid and a *hydriodocantharic acid*, m. p. 172—180°, the "di-iodide," however, not being formed; using hydriodic acid, D 2·0, at 125°, the products are unchanged (or regenerated) cantharidin, cantharic acid, a "*di-iodide*," $C_{10}H_{12}O_3I_2$, colourless crystals, m. p.

117—124° (which, although very similar to Piccard's "di-iodide," appears not to be identical with it), and a mixture of acids, from which a *hydriodocantharic acid*, $C_{10}H_{13}O_4I$, sintering at 128°, m. p. about 140°, has been obtained.

By keeping at the ordinary temperature for six months a mixture of cantharidin, hydriodic acid (D 2·0), and iodine (the last substance is not essential), r-*hydriodocantharic acid*, $C_{10}H_{13}O_4I$, crystals, m. p. 178—180° (decomp.), is obtained. This acid, which is not identical with either of the preceding hydriodocantharic acids, has been resolved by means of the brucine salt. The l-*acid*, colourless needles containing $1H_2O$, m. p. 179—181° (decomp.), has $[\alpha]_D$ − 80° in alcohol ($c = 2$), whilst the d-*acid*, crystals containing $1H_2O$, m. p. 179—181° (decomp.), $[\alpha]_D$ +79—80° ($c = 1·867$), forms two *salts* with brucine, one, $C_{10}H_{14}O_{55}I,2C_{23}H_{26}O_4N_2,7H_2O$, slender needles, decomp. 100—102°, the other, $C_{10}H_{13}O_4I,C_{23}H_{26}O_4N_2,3H_2O$, stout plates, decomp. 111°, sintering at 102° and effloresing rapidly in air.

The action of hydrogen bromide in glacial acetic acid on cantharidin is quite similar to that of hydriodic acid, but a higher temperature is necessary, whilst the reaction with hydrochloric acid only proceeds at a temperature so high (200°) that the characteristic products of the reaction are destroyed.

Cantharidin is not attacked by 21% hydrogen bromide in glacial acetic acid at 100—110°, but at 150—155°, with 13—14% hydrogen bromide, the products, in addition to cantharidin, are cantharic acid, a "*dibromide*," $C_{10}H_{12}O_3Br_2$, crystals, m. p. 133—134° (which can be distilled in a vacuum and, like the "di-iodide," exhibits the behaviour of an acid anhydride during titration), r-*hydrobromocantharic acid*, $C_{10}H_{13}O_4Br$, colourless needles, m. p. 218—220° (decomp.), and a mixture of other acids.

Brucine d-*hydrobromocantharate*, opaque leaflets, containing 3 (or 4) H_2O, m. p. 183—185° (decomp. anhydrous), and *brucine* l-*hydrobromocantharate*, stout, anhydrous crystals, m. p. 222—223° with previous sintering and foaming, yield the active *acids*, $[\alpha]_D$ ±84·4—85·5° in alcohol ($c = 2·28$).

In order to ascertain in what order the products of the action of hydrogen bromide on cantharidin are formed, the three chief products have been separately heated with 13—14% hydrogen bromide in glacial acetic acid at 150—155°: the "dibromide" is practically unchanged and is therefore a final product; the active hydrobromocantharic acids yield *i*-cantharidin, the "dibromide," cantharic acid of the opposite sign to that of the active hydrobromo-acid used, and unchanged and also neutral substances; the active cantharic acids yield unchanged and also neutral substances, and a brominated acid (or acids).

By heating *l*-hydrobromocantharic acid at 215—225° in a current of hydrogen, hydrogen bromide is quantitatively evolved, about one-half of the substance sublimes as cantharidin, and the residue consists of *d*-cantharic acid. C. S.

Cantharic Acid, *iso*Cantharidin, and *iso*Cantharidinic Acid. P. W. Danckwortt (*Arch. Pharm.*, 1914, **252**, 663—682).—Since

cantharic acid is produced from cantharidin and hydrogen haloid owing to the intermediate formation of a hydrohalogencantharic acid (Gadamer, preceding abstract), its formation by Meyer's method (action of chlorosulphonic acid) may be attributed to a similar cause. Attempts to isolate the intermediate product, however, have been unsuccessful, the reaction of cantharidin and an excess of chlorosulphonic acid yielding cantharic acid (89%) and substances free from chlorine.

Phthalide-ω-carboxylic acid contains a group similar to that assumed by Meyer to be present in cantharic acid, but when titrated with *N*/10-potassium hydroxide the two substances behave so differently as to indicate that Meyer's formula must be incorrect.

Cantharic acid, which can be obtained by heating cantharidin with about 10% hydrogen chloride in glacial acetic acid at 200°, has been resolved by means of the brucine salts; the d-*acid*, slender needles, has $[\alpha]_D$ +90·2° in alcohol ($c = 1·6$), whilst the l-*acid*, the brucine salt of which is the more soluble, has $[\alpha]_D$ −72·6°. Attempts to prepare the pure *l*-acid by means of other alkaloids have been unsuccessful.

Anderlini and Ghiro's *iso*cantharidin is best obtained by heating *d*-cantharic acid with acetyl chloride at not above 135°, but if materials containing traces of water or hydrochloric acid are used in its purification the final product appears to be a mixture of *l-iso*cantharidin, *l-iso*cantharidinic acid, and *d*-cantharic acid. C. S.

Cicutoxin: the Poisonous Principle in Water Hemlock (Cicuta). C. A. Jacobson (*J. Amer. Chem. Soc.*, 1915, **37**, 916—934).—An account is given of the extraction and investigation of cicutoxin which has been obtained in a yield of 0·3—0·4% of the weight of the fresh tubers of *Cicuta vagans*. This substance has been described previously by Pohl (A., 1895, i, 681), who obtained it from *C. virosa*.

Cicutoxin, $C_{19}H_{26}O_3$, is an unstable, yellow, resin-like substance which readily decomposes and polymerises, especially at temperatures above 50°, and has D^{22} 0·9659 and n_D^{25} 1·5885; it unites energetically with bromine and ignites spontaneously when a little concentrated nitric acid is dropped on it.

The presence of cicutoxin may be detected by the following test: small quantities of 2% barium hydroxide solution are added to a 5% alcoholic solution of the poison until the voluminous precipitate which is produced becomes pale green; in a few minutes the precipitate darkens to a pea-green or olive-green colour, which subsequently changes to reddish-brown if an excess of barium hydroxide has been used; if a slight excess of mineral acid is now added, the precipitate becomes dark red.

When cicutoxin is submitted to dry distillation, combustible gases are produced together with an oil, $C_{13}H_{21}O_2$, which has D^{20} 0·9360. If the cicutoxin is distilled in a current of steam, it yields a colourless oil, $C_{14}H_{22}O$, which has a pleasant odour and gradually polymerises to a transparent, semi-solid resin. On oxidation with nitric acid, cicutoxin yields carbon dioxide, oxalic acid, hydrogen cyanide, *iso*butyric acid, and acetyl-2-*cyclo*pentanone, b. p. 73·5°/15 mm. By the

action of dilute sulphuric or hydrochloric acid on cicutoxin, a very inert polymerisation *product*, $C_{17}H_{22}O_8$, is produced, whilst on treatment with dilute nitric acid, another *substance*, $C_{15}H_{17}O_8$, is obtained. *Compounds* of cicutoxin with lead, barium, hydrogen chloride, ammonia, bromine, and iodine were prepared and analysed. When a solution of cicutoxin in glacial acetic acid is treated with acetyl chloride, a *compound*, $C_{14}H_{16}O_3Ac_2$, is obtained as a brown powder.

The constitution of cicutoxin is discussed, and evidence is adduced indicating that it is a derivative of 4-pyrone. E. G.

Crystalline Kombé Strophanthin. D. H. Brauns and O. E. Closson (*Arch. Pharm.*, 1914, **252**, 294—340).—The various strophanthins of commerce exhibit different chemical and physiological behaviour. The statements in the literature regarding the seeds of *Strophanthus Kombé* and the Kombé strophanthin obtained from them are very conflicting. One among several reasons for such discrepancies is the not infrequent practice of mixing with the seeds of *Strophanthus Kombé* those of other varieties of *Strophanthus*. The purpose of the present paper is to correct the inaccuracies in the literature and to prepare a strophanthin having constant chemical, physical, and physiological properties.

The seeds of *Strophanthus Kombé* are coarsely powdered, freed from fat by means of light petroleum, and extracted twice with 70% alcohol. The first extract, after being concentrated by evaporation of the alcohol, deposits crystals of strophanthin by keeping. It is preferable, however, to clarify the concentrated extracts with basic lead acetate, and, after removing the lead by hydrogen sulphide, to concentrate the filtrate still further at 40—45°, small quantities of alcohol being occasionally added until the end of the operations, when all the alcohol is removed by distillation. The crystalline Kombé strophanthin thus obtained is purified in a similar manner by solution in alcohol at 40—45°, concentration of the solution, addition of water, and the removal of all alcohol by evaporation. These processes are necessary because strophanthin cannot be crystallised from alcoholic solution, and crystalline strophanthin is readily converted into an amorphous variety by water.

Kombé strophanthin, $C_{40}H_{56}O_{15},3H_2O$, colourless, microscopic needles or plates, has m. p. 158—165° (hydrated) and 178—179° (anhydrous), and $[\alpha]_D + 31{\cdot}6°$ in 94% alcohol (c = about 4) and $+28{\cdot}7°$ in aqueous solution (c = about 0·8), and has a neutral reaction.

The amorphous strophanthin obtained from the crystalline variety by the action of water has the formula $C_{40}H_{58}O_{16}$, is very hygroscopic, has an acid reaction, softens at about 100° in its water of constitution, and then melts at 165—170°; the dried substance has m. p. about 180°, softening at 160°, and has $[\alpha]_D + 20{\cdot}6°$ in aqueous solution (c = about 1·6).

In addition to these two modifications of strophanthin, a third, amorphous variety has been obtained. It is isolated together with the crystalline form from the alcohol extract of the seeds of *Strophanthus Kombé*, and is intimately related to the crystalline form.

All three modifications yield the same strophanthidin by hydrolysis

with dilute mineral acids; this strophanthidin is identical with that obtained by the hydrolysis of Hispidus strophanthin (compare Heffter and Sachs, A., 1912, i, 482). The other product of the hydrolysis has not been definitely identified, but it appears that crystalline Kombé strophanthin does not yield a pentose or a methylpentose (rhamnose), whilst the intimately related amorphous variety yields a pentose.

The second part of the paper deals with the physiological activity of the strophanthins. Tested by Houghton's method, the activities of the crystalline and of the acid, amorphous strophanthins are in the ratio 3 : 1.

A table of references to the literature of the strophanthins since 1873 is given. C. S.

Strophanthus Oil. H. Matthes and L. Rath (*Arch. Pharm.*, 1914, **252**, 683—693).—Strophanthus oil has been thoroughly examined since conflicting statements of its physical and chemical properties have appeared in the literature.

The oil, after being freed by distillation with steam from the light petroleum used in its extraction, and dried over sodium sulphate, has f. p. 16—17°, D^{15} 0·9252, n_D^{40} 1·4615, $\alpha \pm 0°$, acid number 17·61, saponification number 189·99, ester number 172·38, iodine number (Hübl) 94·97, Reichert-Meissl number 1·31, Polenske number 0·59, Hehner number 93·90, yields a positive elaidin reaction, 21% of saturated fatty acids (30% of stearic and 70% of palmitic acid), 73% of unsaturated fatty acids (20% of linolic and 80% of oleic acid), 7·97% of glycerol by hydrolysis, and contains, as stated by Wallenreuter, only one phytosterol, namely, sitosterol, m. p. 137° (acetate, m. p. 127—128°). C. S.

Efficacy of the Digitonin Method for the Isolation of the Sterol in Strophanthus Oil. H. Matthes and L. Rath (*Arch. Pharm.*, 1914, **252**, 694—699).—The sparingly soluble compounds of digitonin and sterols (Windaus, A., 1909, i, 172) have frequently been employed for the rapid isolation of the sterols in fats (Matthes and Dahle, A., 1911, i, 858; Marcusson and Schilling, A., 1913, ii, 885; Klostermann, A., 1914, ii, 79). The last method is cumbersome but quantitative, Marcusson and Schilling's simple but not quantitative; both yield pure steryl acetates.

Before applying the method to strophanthus oil, the authors examined the behaviour of the pure phytosterol, obtained from the oil, with digitonin in hot alcohol; the *digitonin-phytosteride* crystallises almost immediately. It decomposes at 245°, and exhibits the following phytosterol reactions: Liebermann-Burchard, rose, violet, blue; Tschugaev, yellowish-red, green fluorescence; Udranski, red, greenish-yellow, dirty brown.

When applied to an alcoholic solution of the unsaponifiable constituents of the oil, the method detected 58% of the mixture as a phytosterol, whereas the customary process gave 60%. The phytosterol, in the form of the acetate, m. p. 127—128° (preceding abstract), has been isolated from the saponified oil by Klostermann's method, and from the

unsaponified oil by that of Marcusson and Schilling; the yields are not recorded. C. S.

Unsaponifiable Constituents of Strophanthus Oil. A. Heiduschka and R. Wallenreuter (*Arch. Pharm.*, 1914, **252**, 704—708). —The oil is saponified and extracted with ether. The residue from the ethereal extract is again saponified and treated with ether to isolate the unsaponifiable constituents, the yield of which is 1·12%. The amount of the phytosterol, estimated by Windaus's digitonin method, is 0·504%, calculated on the original oil. The *phytosterol*, $C_{27}H_{46}O$, colourless crystals containing $\frac{1}{2}$ or $1H_2O$, m. p. 140°, forms an *acetate*, m. p. 130°, and *propionate*, m. p. 111°, and is individual, its acetate yielding by bromination in glacial acetic acid only sitosteryl acetate dibromide. C. S.

Tannin and the Synthesis of Similar Substances. IV. Emil Fischer and Karl Freudenberg (*Ber.*, 1914, **47**, 2485—2504. Compare A., 1912, i, 471, 887; 1913, i, 479).—The authors accept the statement of Feist and Haun (A., 1912, i, 888; 1914, i, 195) as to the distinct nature of tannin from Turkish and Chinese galls, but do not consider their other conclusions with favour.

Using Aleppo galls the authors have endeavoured in vain to isolate the glucogallic acid described by Feist and Haun as obtainable from Turkish galls, and question the nature of the product obtained by the latter workers; in place of glucogallic acid, a mixture of gallic acid and tannin was obtained. Tannin from Turkish galls has been purified by the ethyl acetate method, and on hydrolysis by sulphuric acid is found to yield dextrose and gallic acid together with ellagic acid; the last substance appears to be absent from Chinese tannin, thus confirming the view, suggested by other facts, that Chinese tannin is less complex than Turkish. As the proportion of dextrose to gallic acid obtainable from Turkish tannin is higher than that in the mixture from the Chinese product, the possibility of the presence of a pentagalloylglucose as an essential constituent is considered, and for purposes of comparison a pentagalloyl derivative of β-glucose was desirable.

Pure β-glucose was coupled with trimethylcarbonatogalloyl chloride in cold chloroform solution containing quinoline, and the resulting *β-penta[trimethylcarbonatogalloyl]glucose* was precipitated by pouring the reaction mixture into methyl alcohol; the product had $[\alpha]_D^{15}$ + 6·10° (in *s*-tetrachloroethane), and was therefore distinct from the substance already described as the α-isomeride ($[\alpha]_D$ + 343°), but on hydrolysis with cold alkali a product was obtained so similar in optical activity to that derived from the α-isomeride as to render it probable that both consisted of the same galloylglucose; this result is to be referred either to the isomerising effect of the alkali or to the product of hydrolysis being a tetragalloylglucose instead of a pentagalloyl derivative; the former view is preferred.

Both α- and β-glucose have been condensed with trimethylgalloyl chloride in cold chloroform solution containing quinoline, the products being the α- and β-isomerides respectively of *penta[trimethylgalloyl-*

glucose]. The former isomeride was an amorphous solid, m. p. indistinct at 98—99°, $[\alpha]_D^{19}$ +70·04° (in *s*-tetrachloroethane), whilst the *β*-compound, m. p. 133—134° (corr.), $[\alpha]_D^{23}$ +17·18° (in *s*-tetrachloroethane), was obtained crystalline, and is indeed the first synthetic substance of the tannin group produced in a crystalline condition.

The action of diazomethane on Turkish tannin gave a product the hydrolysis of which yielded a little *mp*-dimethylgallic acid with a preponderating amount of trimethylgallic acid; the phenolic hydroxyl groups are therefore almost entirely free in Turkish tannin, and the galloyl groups must therefore be present almost entirely as such and not in the form of condensed groups, such as digalloyl. D. F. T.

Peptonisation Phenomena in Solutions of Tanning Substances. W. MOELLER (*Kolloid. Zeitsch.*, 1915, **16**, 69—76).—The nature of tanning solutions and of the tanning process is discussed and a theory is suggested according to which these solutions contain peptonised colloids which are coagulated in contact with hide substance. The conclusions drawn by the author from an investigation of the properties of solutions of tanning substances of the most various kinds, is that all these solutions contain peptonised gels, and also a substance which acts as peptoniser. True solutions have no tanning properties. In the tanning process, the peptoniser is absorbed by the hide substance, and this results in the coagulation of the gel which is deposited on the skin fibres. The properties of the different tanning substances are dependent on the equilibrium between the peptoniser and the peptonised gel, and the properties of the tanned hide on the nature and quantity of the coagulated gel which separates out on the fibres. In so far as the resulting leather is concerned, the peptoniser is only of secondary importance. H. M. D.

Resorcinolbenzein. HANS VON LIEBIG (*Ber.*, 1914, **47**, 2592—2598. Compare A., 1912, i, 376).—A reply to the views of Kehrmann and Loth (A., 1914, i, 1082) and Pope (T., 1914, **105**, 251) as to the non-existence of the *α*, *β*, *γ* and *δ* forms of resorcinolbenzein described by the author (*loc. cit.*). D. F. T.

Constituents of the Kawa-root. I. Yangonin. W. BORSCHE and MATHILDE GERHARDT (*Ber.*, 1914, **47**, 2902—2918).—An investigation of yangonin, a constituent of kawa-root (*Piper methysticum*), and related substances. Catalytic hydrogenation by Paal's method converts yangonin into dihydroyangonin, indicating the presence of an ethylene linking. On saponification, yangonin yields anisaldehyde and *p*-methoxycinnamic acid. Owing to the absence of a double linking, similar treatment converts dihydroyangonin into *p*-methoxyphenylethyl methyl ketone and *p*-methoxyphenylpropionic acid. The formation of anisaldehyde is probably due to further degradation of anisylideneacetone, $C_{11}H_{12}O_2$.

Yangonic acid, $C_{14}H_{14}O_5$, is related to anisylideneacetone [*p*-methoxystyryl methyl ketone], and is probably *γ*-*p*-methoxycinnamoylacetoacetic acid, $OMe\cdot C_6H_4\cdot CH{:}CH\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot CO_2H$. The trans-

formation of yangonin into yangonic acid involves replacement of methoxyl by hydroxyl and the addition of the elements of water, indicating yangonin to be the anhydride of methyl yangonate in its enolic form, that is, 2-methoxy-6-*p*-methoxystyryl-4-pyrone. In accordance with this view it combines with acids to form oxonium salts, and with ammonia to form a 4-pyridone.

Alkaline hydrolysis transforms 2 : 6-dimethyl-4-pyrone into *s*-diacetylacetone, this product being then converted into either acetylacetone and acetic acid, or acetone and acetoacetic acid (or two molecules of acetic acid). In an analogous manner the hydrolysis of yangonin yields first yangonic acid and then either *p*-methoxycinnamic acid and acetoacetic acid or anisylideneacetone (anisaldehyde and acetone) and malonic acid. For dihydroyangonin the corresponding products are dihydroyangonic acid, *p*-methoxydihydrocinnamic acid and acetoacetic acid, or anisylacetone and malonic acid.

The formation of the oxonium salts of yangonin is much facilitated by the weak additive nature of the ethylene linking, exemplified by the labile character of yangonin dibromide. Double compounds of yangonin hydrochloride with such metallic chlorides as ferric, auric, and platinic chlorides were obtained. The oxonium salts of dihydroyangonin have not been fully investigated.

An attempt to synthesise 6-*p*-methoxyvstvryl-2-methyl-4-pyrone, a compound of the yangonin-type, by the condensation of dehydroacetic acid and anisaldehyde to anisylidenedehydroacetic acid and the transformation of this product by means of fuming hydrochloric acid, proved unsuccessful.

Yangonin, $CH\begin{matrix}\ll C(OMe)\cdot O\\ CO---CH\end{matrix}\gg C\cdot CH{:}CH\cdot C_6H_4\cdot OMe$, forms pale greenish-yellow prisms, m. p. 154°. In the residues from the preparation of kawa-resin it is associated with methysticin, and can be purified by repeated extraction with boiling acetone and crystallisation from glacial acetic acid. On saponification it yields anisaldehyde and *p*-methoxycinnamic acid.

Yangonin ferrichloride, $2C_{15}H_{14}O_4,HCl,FeCl_3$, forms steel-blue, glistening needles, m. p. 151° (decomp.). The *aurichloride*,

$$2C_{15}H_{14}O_4,AuCl_4,$$

crystallises in yellowish-red needles, m. p. 154° (decomp.). The *platinichloride* crystallises with acetic acid in orange crystals,

$$2C_{15}H_{14}O_4,H_2PtCl_6,C_2H_2O_4,$$

m. p. 168—169°.

A greenish-yellow powder, m. p. 164—165° (decomp.), formed by the action of bromine on yangonin, is possibly *yangonin dibromide hydrobromide*. Crystallisation from alcohol decomposes it into two isomeric *monobromoyangonins*, $C_{15}H_{13}O_4Br$, the less soluble forming yellow leaflets, m. p. 186—188°, and the other similar crystals, m. p. 175—176°. When yangonin dibromide hydrobromide is boiled with pyridine, it yields several bromo-derivatives, and also a *substance* free from bromine, yellow leaflets or needles, m. p. 276—277°. The constitution of these substances is uncertain.

6-*Hydroxy*-1-p-*methoxystyryl*-4-*pyridone* can be isolated from the reaction product of yangonin and concentrated aqueous ammonia at

150°, the solution being evaporated to a resin, which is extracted with ammonium hydroxide, and thrown down with dilute hydrochloric acid as a bulky, yellow precipitate. It decomposes without melting below 330°.

Dihydroyangonin, $C_{15}H_{16}O_4$, obtained by hydrogenation of yangonin, crystallises in thick, white needles, m. p. 106—107°. On saponification with potassium hydroxide, it is converted into *potassium dihydroyangonate*, colourless leaflets, from which acid liberates *dihydroyangonic acid*, needles, m. p. 76—77°. Further action of alkali on dihydroyangonin produces anisylideneacetone and *p*-methoxyphenylpropionic acid. Concentrated aqueous ammonia does not resinify dihydroyangonin, but transforms it into 6-*amino*-2-p-*methoxyphenylethyl*-4-*pyridone*, $C_{14}H_{16}O_2N_2$, white needles, m. p. 235°, traces of the corresponding hydroxy-derivative, $C_{14}H_{15}O_3N$, anisylacetone, and p-*methoxydihydrocinnamide*, colourless leaflets, m. p. 125—126°. An impure specimen of the hydroxy-compound melted at 330°. It is probably 6-*hydroxy*-2-p-*methoxyphenylethyl*-4 *pyridone*. *Anisylidenedehydroacetic acid* forms orange plates, m. p. 203—204°. A. J. W.

Ring Opening and Closing with Derivatives of Coumaranones and of Phenyl Methyl Diketone and Desmotropy of Such Compounds. K. VON AUWERS (*Ber.*, 1914, **47**, 3292—3326).—1-Alkylcoumaranones (or 2-hydroxy-1-alkylcoumarones) react with semicarbazide to yield mixtures of monosemicarbazones insoluble in alkali and substances which dissolve in alkali, and are formed by the action of two molecules of semicarbazide. The behaviour is not shown by coumaranone itself or by 1 : 1-dialkylcoumaranones (compare A., 1910, i, 629; 1912, i, 484; 1914, i, 1136). This peculiarity has been investigated more fully in the case of 1 : 4-dimethylcoumaranone. The nature of its disemicarbazone, m. p. 225—226° (A., 1912, i, 484), has not been definitely established, but it appears, according to the following evidence, to have the formula $OH\cdot C_6H_3Me\cdot C(:N\cdot NH\cdot CO\cdot NH_2)\cdot CMe:N\cdot NH\cdot CO\cdot NH_2$. By hydrolysis with concentrated hydrochloric acid it yields a *substance*, colourless needles, m. p. 108—109°, which appears to be 1-hydroxy-1 : 4-dimethylcoumaran-2-one, since it can be prepared from 3-propionyl-*p*-cresol and yields *p*-homosalicylic acid by oxidation. By treatment with methyl sulphate and sodium hydroxide, the disemicarbazone, m. p. 225—226°, yields the *disemicarbazone*, m. p. 239°, of the *methyl ether*, m. p. 60—61°, obtained by the hydrolysis of 3-*oximinopropionyl*-p-*tolyl methyl ether*, $OMe\cdot C_6H_3Me\cdot CO\cdot CMe:NOH$, pale yellow needles, m. p. 91°. The methyl ether, m. p. 60—61°, is regarded as having the constitution $OMe\cdot C_6H_3Me\cdot CO\cdot COMe$. It yields the substance, m. p. 108—109°, by demethylation. Isomeric with the methyl ether, m. p. 60—61°, is the *methyl ether*, b. p. 139—142°/18—19 mm., D_4^{20} 1·132, n_D^{20} 1·5394, obtained directly from the substance, m. p. 108—109°. The liquid ether probably has the constitution

$$C_6H_3Me\langle\begin{matrix}CO\\-O-\end{matrix}\rangle CMe\cdot OMe,$$

since it and the corresponding ethyl ether yield the same disemicarb-

azone by a series of changes involving the opening of the furan ring and the elimination of the alkyloxy-group.

1-Hydroxy-1 : 4-dimethylcoumaran-2-one forms an *acetate*, m. p. 85—86°, and *benzoate*, colourless needles, m. p. 119—120°, and is readily reconverted into the disemicarbazone, m. p. 225°, which is the sole product even when less than 1 mol. of semicarbazide is employed. With *p*-nitrophenylhydrazine, it yields a mixture of *mononitrophenylhydrazone*, golden needles, m. p. 175—176°, and *osazone*. 1-*Bromo*-1 : 4-*dimethylcoumaranone*, m. p. 63—64°, is best obtained by the action of bromine on dimethylcoumaranone in carbon disulphide solution; hydrogen bromide is not immediately evolved, but attempts to isolate the probable additive product,

$$C_6H_3Me\langle\begin{matrix}C(OH)Br\\ \text{---}O\text{---}\end{matrix}\rangle CBrMe,$$

were unsuccessful. 1-Hydroxy-1 : 4-dimethylcoumaranone is formed by hydrolysis of the bromide or of the *acetyl* derivative, m. p. 85—86°, obtained by the action of silver or potassium acetate on the bromo-compound. 1-Methoxy-1 : 4-dimethylcoumaranone, obtained from the bromo-compound and sodium methoxide, is identical with the product obtained by methylating hydroxydimethylcoumaranone. 1-*Ethoxy*-1 : 4-*dimethylcoumaranone* has b. p. 145·5—146°/17—18 mm., $D_4^{18\cdot4}$ 1·0996, D_4^{20} 1·098, $n^{18\cdot3}$ 1·52381, $n_D^{18\cdot3}$ 1·52999, $n_\beta^{18\cdot3}$ 1·54712, $n_\gamma^{18\cdot3}$ 1·56588, n_D^{20} 1·5292.

Small quantities of *o*-propionyl-*p*-cresol and of its methyl ether are conveniently prepared by methylation of *p*-cresol and treatment of the product with propionyl chloride and aluminium chloride in carbon disulphide solution. Larger quantities are better obtained by converting *p*-cresol into its propionic ester by the action of phosphoryl chloride and propionic acid, transforming the ester by treatment with aluminium chloride into propionyl-*p*-cresol and methylation of the latter. *o*-Propionyl-*p*-cresol has b. p. 123—124°/11 mm., 129—130°/16·5 mm. Its methyl ether boils at 134—136°/10 mm., 145—146·5°/16·5 mm., whereas Klages (A., 1904, i, 1001) gives 149—151°/17 mm.

The methyl ether, m. p. 60—61°, mentioned above, forms an *α-p-nitrophenylhydrazone*, $OMe\cdot C_6H_3Me\cdot C(:N\cdot NH\cdot C_6H_4\cdot NO_2)\cdot COMe$, yellow needles, m. p. 212—213°, an *osazone*,

$$OMe\cdot C_6H_3Me\cdot C(:N\cdot NH\cdot C_6H_4\cdot NO_2)\cdot CMe:N\cdot NH\cdot C_6H_4\cdot NO_2,$$

red needles, m. p. above 280°, and a *dioxime*, m. p. 201—202°.

o-Propionyl-*p*-cresol forms a *benzoate*, prisms, m. p. 96—97°, from which the corresponding *oximino*-compound,

$$OBz\cdot C_6H_3Me\cdot CO\cdot CMe:NOH,$$

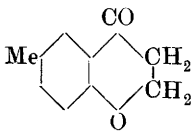
needles, m. p. 126—127°, is obtained by the action of amyl nitrite and concentrated hydrochloric acid. The latter is readily transformed in alkaline solution into the *β-oxime* of *hydroxy*-p-*tolyl methyl diketone*, prisms, m. p. 90·5—91·5°. The elimination of the oximino-group from the benzoate is a matter of difficulty; the most favourable results are obtained by the action of ethyl nitrite and concentrated hydrochloric acid, whereby small quantities of the *benzoate*, $OBz\cdot C_6H_3Me\cdot CO\cdot COMe$, colourless needles, m. p. 149·5—150·5°, are produced.

o-*α-Bromopropionyl-p-tolyl benzoate*, $OBz\cdot C_6H_3Me\cdot CO\cdot CHMeBr$,

needles or prisms, m. p. 107—108°, is obtained by the action of benzoyl chloride on bromopropionyl-*p*-cresol at 165—175°. H. W.

6-Methylchromanone. K. VON AUWERS and F. KROLLPFEIFFER (*Ber.*, 1914, **47**, 2585—2591).—For the purpose of a spectrochemical investigation, "chromanone," $C_6H_4<^{CO\cdot CH_2}_{O---CH_2}$, or a simple homologue was required; a compound of the desired type has been obtained by the synthesis of 6-methylchromanone.

By condensation of *p*-tolyl methyl ether with *β*-iodopropionyl chloride in carbon disulphide in the presence of freshly prepared aluminium chloride, o-*β-iodopropionyl*-p-*cresol*, $OH\cdot C_6H_3Me\cdot CO\cdot CH_2\cdot CH_2I$, colourless needles, m. p. 65—66°, is obtained. When heated in aqueous-alcoholic solution with sodium hydroxide, this substance undergoes ring formation with production of 6-*methylchromanone* (annexed formula), colourless prisms, m. p. 34—36°; *semicarbazone*, colourless prisms, m. p. 248—249°, if rapidly heated; *oxime*, colourless needles, m. p. 84—85°; p-*nitrophenylhydrazone*, orange-red needles, m. p. 222°.



Bromination in carbon disulphide solution converts 6-methylchromanone into 3-*bromo*-6-*methylchromanone*, $C_6H_3Me<^{CO\cdot CHBr}_{O---CH_2}$, colourless needles, m. p. 74°, which on boiling with a solution of potassium acetate in acetic acid and with sodium carbonate solution respectively yields a substance, probably the *acetate* of 3-hydroxy-6-methylchromanone and a red *sodium* salt; the latter on acidification gave its parent *substance*, colourless leaflets, m. p. 186—188°; these products were not further examined. It was not found possible to eliminate hydrogen bromide from the bromomethylchromanone, and so to obtain the already known 6-methylchromone, $C_6H_3Me<^{CO\cdot CH}_{O---CH}$.

6-Methylchromanone condenses with benzaldehyde, giving 3-*benzylidene*-6-*methylchromanone*, $C_6H_3Me<^{CO\cdot C:CHPh}_{O---CH_2}$, pale yellow leaflets, m. p. 147—148°, and reacts with magnesium methyl iodide giving 4 : 6-*dimethyldihydro*-4-*chromanol*, $C_6H_3Me<^{CMe(OH)\cdot CH_2}_{O---------CH_2}$, colourless rhombohedra, m. p. 116—117°. When heated at 80° with phosphorus pentoxide in a vacuum, this substance underwent dehydration to 4 : 6-*dimethylchromene*, $C_6H_3Me<^{CMe:CH}_{O---CH_2}$, a colourless oil, b. p. 124°/13 mm., D_4^{20} 1·042; this is a typical chromene, having the characteristic odour and becoming violet when exposed to light.

D. F. T.

Syntheses of γ-Benzopyrones and Flavones. I. SERGE JACOBSON and BROJENDRANATH GHOSH (T., 1915, **107**, 424—434).—The condensation of ethyl acetoacetate with phenols to form coumarins seems to be regarded as a general reaction. Bülow and Wagner

(A., 1901, i, 400) have shown that *m*-dihydroxyphenols condense with acetyl- or benzoyl-acetone to form methylene-substituted pyrones; Collie and White have obtained similar compounds from orcinol and acetylacetone. It was therefore considered of interest to study the condensation of phenols with acetoacetic esters in order to ascertain whether pyrone compounds are produced in such reactions. In the case of non-substituted and methyl-substituted acetoacetic esters, coumarins are produced, whilst with ethyl ethylacetoacetate a mixture of a γ-benzopyrone and a coumarin is obtained. Ethyl benzylacetoacetate yields γ-benzopyrones.

An account is given of the behaviour of ethyl benzylacetoacetate with resorcinol, *m*-cresol, pyrogallol, orcinol, phloroglucinol, and α-naphthol in presence of sulphuric acid. The condensation proceeds well with *m*-dihydroxyphenols, but with other phenols only small yields are obtained; *p*-cresol does not give a condensation product. In all cases, a small quantity of methylindenecarboxylic acid is formed by the internal condensation of ethyl benzylacetoacetate.

7-*Hydroxy*-3-*benzyl*-2-*methyl*-γ-*benzopyrone*,

$$OH\cdot C_6H_3\begin{cases}O-C\ Me\\ CO\cdot C\cdot CH_2Ph\end{cases},\tfrac{1}{2}H_2O,$$

m. p. 186°, from resorcinol and ethyl benzylacetoacetate, forms long, yellow needles; its *acetyl* derivative, m. p. 168°, crystallises in long, silky needles, containing $\frac{1}{2}H_2O$, and its *benzoyl* derivative, m. p. 150°, forms soft, long needles. The *methyl ether*, m. p. 119°, and the *ethyl ether*, m. p. 145°, crystallise in needles. Both the pyrone itself and its ethers yield a bluish-violet fluorescence in concentrated sulphuric acid. On hydrolysis with potassium hydroxide, the pyrone furnishes benzylacetone and β-resorcylic acid. When the pyrone is fused with phosphorus pentasulphide, a *thio*-derivative, $C_{17}H_{14}OS_2$, m. p. 198° (decomp.), is obtained in the form of brick-red prisms.

If, in the condensation of resorcinol with ethyl benzylacetoacetate, a smaller quantity of sulphuric acid is employed, 7-*hydroxy*-3-*m*-*hydroxyphenoxy*-3-*benzyl*-2-*methyl*-γ-*benzopyrone*,

$$OH\cdot C_6H_3\begin{cases}O-CHMe\\ CO\cdot C(CH_2Ph)\cdot O\cdot C_6H_4\cdot OH'\end{cases}$$

m. p. 224°, is produced, which forms short, yellow, glistening prisms and gives a bluish-violet fluorescence when heated with sulphuric acid; when boiled with acetic anhydride and sodium acetate, it yields the acetyl derivative of 7-hydroxy-3-benzyl-2-methyl-γ-benzopyrone.

By the condensation of *m*-cresol with ethyl benzylacetoacetate, 3-benzyl-2:7-dimethyl-γ-benzopyrone, $C_{19}H_{16}O_2$, m. p. 117°, is produced which was regarded by Fries and Klostermann (A., 1908, i, 822) as a coumarin; on hydrolysis it yields benzylacetone. On attempting to prepare the compound obtained by Fries and Klostermann (*loc. cit.*) from *m*-cresol and ethyl ethylacetoacetate, a *product*, $C_{20}H_{22}O_3$, was obtained, m. p. 130° (instead of 87°), which appears to be an additive compound of Fries and Klostermann's substance with 1 mol. of *m*-cresol.

3-*Benzyl*-2-*methyl*-1:4-α-*naphthapyrone*, $C_{21}H_{16}O_2$, m. p. 187°, from α-naphthol and ethyl benzylacetoacetate, forms yellow needles and, on

hydrolysis, is converted into benzylacetone and 1-naphthol-2-carboxylic acid.

7 : 8-*Dihydroxy-3-benzyl-2-methyl-γ-benzopyrone*, $C_{17}H_{14}O_4,H_2O$, m. p. 185°, from pyrogallol and ethyl benzylacetoacetate, gives a green fluorescence in concentrated sulphuric acid; its *acetyl* derivative, m. p. 172°, crystallises in white prisms, and its *benzoyl* derivative, m. p. 184°, in needles.

7-*Hydroxy-3-benzyl-2* : 5-*dimethyl-γ-benzopyrone*, $C_{18}H_{16}O_3$, m. p. 177—178°, from orcinol and ethyl benzylacetoacetate, forms short, white needles; its *acetyl* and *benzoyl* derivatives have m. p. 169° and 119—120° respectively.

5 : 7-*Dihydroxy-3-benzyl-2-methyl-γ-benzopyrone*, $C_{17}H_{14}O_4\cdot\frac{1}{2}H_2O$, m. p. 218—219°, from phloroglucinol and ethyl benzylacetoacetate, crystallises in hard, short needles; its *acetyl* derivative, m. p. 154°, forms long, silky needles. E. G.

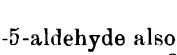
Action of Magnesium Ethyl Iodide on Ethyl α-Thienyl Ketone. (Mlle.) E. Domratscheva (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 864—867. Compare Thomas, A., 1908, i, 360).—2-*Thienyldiethylcarbinol*, $OH\cdot CEt_2\cdot C\begin{matrix}CH\cdot CH\\ \| \\ S---CH\end{matrix}$, obtained by the action of magnesium ethyl iodide on ethyl α-thienyl ketone in ethereal solution, is a viscous, colourless liquid with a characteristic odour, and forms a solid, transparent mass when cooled in solid carbon dioxide and ether, b. p. 116—117°/18 mm., $D_4^{14\cdot5}$ 1·0779, $n_D^{14\cdot5}$ 1·5293. In freezing benzene it has the molecular weight 141—145, instead of 170. When heated at 120° with a mixture of equal weights of alcohol and anhydrous oxalic acid, it loses the elements of water, yielding: (1) γ-2-*thienyl-Δ^β-pentene*, $CHMe{:}CEt\cdot C_4H_3S$, which is a liquid of characteristic odour, solidifying to a vitreous mass at −80°, b. p. 90—91·5°/16 mm., $D_4^{19\cdot4}$ 1·0079, $n_D^{19\cdot4}$ 1·5502. It combines with bromine (2 atoms), giving an unstable compound, and when oxidised with permanganate gives thiophen 2-carboxylic acid in small yield. (2) A *dimeride* of (1), $C_{18}H_{24}S_2$, which is a very viscous, yellow liquid, b. p. 213—218°/16 mm., D_4^{22} 1 0770, n_D^{22} 1·5815, and has the molecular weight 264, instead of 304, in freezing benzene. T. H. P.

2-Methylthiophen, 5-Iodo 2-methylthiophen, and 2-Methylthiophen 5-aldehyde. (Mlle.) Anna Vlastelica (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 790—800).—5-Iodo-2-methylthiophen (compare Grishkevitsch-Trochimovski, A., 1911, i, 481), prepared by the action of iodine and yellow mercuric oxide on 2-methylthiophen in benzene solution, is a yellow, oily liquid with a characteristic, pleasant odour, b. p. 94°/16—17 mm., D_4^{20} 1·8794, D_4^{23} 1·8749, D_4^{24} 1·8734, n_D^{20} 1 62304, coefficient of surface tension $\gamma^{20\cdot6}$ 4·2535.

The *azine* of *2-methylthiophen-5-aldehyde*, $C_{12}H_{12}N_2S_2$, forms yellow crystals, m. p. 135·4—136°. With ammonia and ethyl acetoacetate, 2-methylthiophen-5-aldehyde condenses, forming *ethyl 4-methylthienyl-2* : 6-*dimethyldihydropyridine* 3 : 5-*dicarboxylate*,

$$C_5H_5S\cdot CH\begin{matrix}C(CO_2Et){:}CMe\\ C(CO_2Et){:}CMe\end{matrix}NH,$$

which forms white, acicular crystals, m. p. 148—148·4°.

2-Methylthiophen-5-aldehyde also condenses: (1) with styryl methyl ketone, giving the *compound*,  , which forms yellow, acicular crystals, or rosette-like aggregates, m. p. 58·5—60·50°, with red and green reflection; with concentrated sulphuric or hydrochloric acid, a trace of the ketone gives a blood-red coloration, which disappears on dilution with water; (2) with dimethylaniline, giving *tetramethyldiaminodiphenylmethylthienylmethane*, $C_5H_5S\cdot CH(C_6H_4\cdot NMe_2)_2$, which forms white, acicular crystals, m. p. 131·4—131·8°, and in alcoholic solution is oxidised by the air, giving an intense, green coloration.

Tetramethyldiaminodiphenylmethylthienylcarbinol,

$$C_5H_5S\cdot C(OH)(\cdot C_6H_4\cdot NMe_2)_2,$$

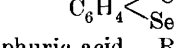
prepared by the action of tetramethyldiaminobenzophenone on magnesium methylthienyl iodide, followed by decomposition of the complex organo-magnesium compound, forms a pale grey, indistinctly crystalline powder, blackening at 130° and completely charring at a higher temperature. Solutions of its sulphate and hydrochloride, which are hydrolysed by water with separation of the base, dye silk and wool raspberry-red, this being changed to a bright bluish-green by the action of water; very dilute solutions dye textiles bright blue. The dye is fast against water and soap. With zinc chloride, the hydrochloride of the base forms the *double* salt,

$$3C_4H_5S\cdot C(C_6H_4\cdot NMe_2)(:C_6H_4:NMe_2Cl),2ZnCl_2,3H_2O,$$

which forms brown crystals with the lustre of copper and blackens at 150° and carbonises completely at about 200°; its alcoholic solution is bluish-violet. Textiles dyed by means of this double salt exhibit a marked blue tint, which distinguishes them from those coloured with thiophen-green. T. H. P.

Aromatic Selenium Compounds. V. Selenoxanthone and Selenoxanthonecarboxylic Acid. R. Lesser and R. Weiss (*Ber.*, 1914, **47**, 2510—2526. Compare this vol., i, 404).—In their account of diphenylselenide-di-*o*-carboxylic acid (A., 1913, i, 1184) the authors have described the production of selenoxanthonecarboxylic acid and a neutral substance, believed to be benzophenoneselenone,

$$C_6H_4<\begin{matrix}CO\\SeO_2\end{matrix}>C_6H_4,$$

by the action of sulphuric acid. Repetition of the investigation on a larger scale, however, shows the neutral compound to be a *dilactone*,  , derived from the hypothetical diphenylselenoxide-di-*o*-carboxylic acid, or its corresponding dihydroxy-compound,

$$CO_2H\cdot C_6H_4\cdot Se(OH)_2\cdot C_6H_4\cdot CO_2H.$$

The action of sulphuric acid was therefore one of oxidation and not of condensation.

Diphenylselenidedi-*o*-carboxylic acid was prepared by the interaction of sodium *o*-iodobenzoate and a solution of sodium *o*-selenolbenzoate; when treated for four or five hours with ten times its weight of

sulphuric acid it gives a mixture of selenoxanthonecarboxylic acid and the above dilactone, the relative proportion of the latter increasing with the temperature of the reaction. The dilactone forms colourless needles, m. p. 323—325° (decomp.); on reduction with zinc dust and an alkali hydroxide or acetic acid it is reconverted into diphenylselenidedi-*o*-carboxylic acid.

The following derivatives of selenoxanthonecarboxylic acid,

$$C_6H_4\langle\begin{matrix}CO\\Se\end{matrix}\rangle C_6H_3\cdot CO_2H,$$

are described: *potassium* salt, yellow; *barium* salt, yellow needles; the *chloride*, yellow needles, m. p. 220—221°, was allowed to react with various normal paraffin alcohols with the formation of various esters, which were all of a pale yellow colour; *methyl* ester, needles, m. p. 180—181°; *ethyl* ester, needles, m. p. 162—163°; *propyl* ester, microscopic needles, m. p. 126—127°; *butyl* ester, cubic crystals, m. p. 116—117°; *amyl* ester, needles, m. p. 73—74°; *hexyl* ester, needles, m. p. 82—83°; *heptyl* ester, pyramidal crystals, m. p. 70—71°; *octyl* ester, needles, m. p. 74—75°; *nonyl* ester, prisms, m. p. 74·5—75·5°; *decyl* ester, needles, m. p. 68—69°; *undecyl* ester, microscopic tablets, m. p. 75·5—76·5°; *dodecyl* ester, crystals, m. p. 66—67°; *tetradecyl* ester, needles, m. p. 72·5—73·5°; *hexadecyl* (*cetyl*) ester, needles, m. p. 63—64°; *octadecyl* ester, needles, m. p. 83·5—84·5°. Some of the higher alcohols were prepared by reduction of the corresponding fatty acids with sodium, and in connexion with this work *methyl undecoate* was obtained as a pleasant smelling liquid, b. p. 123°/9—10 mm. Other derivatives prepared from selenoxanthonecarboxylic acid were the *amide*, yellow needles, m. p. 263—264°, and the *anilide*, pale yellow needles, m. p. 270—271°.

When selenoxanthonecarboxylic acid is heated with quicklime, *selenoxanthone*, $C_6H_4\langle\begin{matrix}CO\\Se\end{matrix}\rangle C_6H_4$, is obtained. This substance, which forms pale yellow needles, m. p. 191—192°, can be prepared more conveniently by intramolecular condensation of *diphenylselenide-o-carboxylic acid*, $CO_2H\cdot C_6H_4\cdot Se\cdot C_6H_5$, in the presence of sulphuric acid. The necessary carboxylic acid is producible by the interaction of selenolbenzene and diazotised anthranilic acid and forms colourless crystals, m. p. 189—190°; *potassium* and *sodium* salts, colourless needles; *barium* salt, amorphous; acid *chloride*, crystals, m. p. 72—73°; *methyl* ester, rods, m. p. 71—72°; *amide*, needles, m. p. 201—202°; *anilide*, needles, m. p. 145·5—146·5°. Selenoxanthone shows marked similarity to thioxanthone, but differs from it in its behaviour on oxidation. Whereas the latter substance readily yields benzophenonesulphone, selenoxanthone is resistant to nitric acid (D 1·4), and with chromic acid in acetic acid solution gives an additive compound, $C_{13}H_8OSe,CrO_3$, orange-yellow prisms, which undergoes partial decomposition under the action of water. When boiled with dilute alkalis, a chromate is produced together with a colourless *substance*, leaflets or needles, m. p. 230—231°, at which temperature it undergoes re-conversion into selenoxanthone with loss of the elements of water.

D. F. T.

Angostura Alkaloids. Isomerisation and Degradation of Cusparine. J. TRÖGER and W. MÜLLER (*Arch. Pharm.*, 1914, **252**, 459—496).—The main object of the investigation is to prove that *iso*cusparine, m. p. 194°, the substance obtained by Tröger and Beck (A., 1913, i, 748) from cusparine methiodide, ethiodide and propiodide, is not a demethylated cusparine, but an isomeride in which the methyl group has migrated from an oxygen atom to the nitrogen atom. Thirty-four analyses of *iso*cusparine from the three sources and 7 of its platinichloride furnish strong, but not conclusive, evidence of the formula $C_{19}H_{17}O_3N$ rather than $C_{18}H_{15}O_3N$.

It is now shown that *iso*cusparine is formed by heating cusparine methiodide at 196° in a current of carbon dioxide, methyl iodide being evolved. *iso*Cusparine is also obtained by heating cusparine in a current of methyl iodide vapour at 120—191°, or of ethyl iodide vapour at 153—198°; the former of these two methods is the best and simplest process of converting cusparine into *iso*cusparine, the yield being about 90%.

Tested by the Zeisel method, *iso*cusparine does not contain a methoxyl group. This does not prove that it is a demethylated cusparine, because it is not identical with pyrocusparine,

$$C_{18}H_{15}O_3N,$$

m. p. 255°, which is produced by demethylating cusparine by hydrogen chloride.

Good evidence of the formula $C_{19}H_{17}O_3N$ (as against $C_{18}H_{15}O_3N$) for *iso*cusparine is obtained by the analysis of the *hydriodide*,

$$C_{19}H_{17}O_3N,HI,H_2O,$$

sulphur-yellow needles. *Cusparine hydriodide*, $C_{19}H_{17}O_3N,HI$, yellow crystals, regenerates cusparine by treatment with alkali, but is decomposed into pyrocusparine and methyl iodide by heating at 180—190° in a current of carbon dioxide.

The presence of one methylimino-group in *iso*cusparine is proved by the method of Herzig and Meyer, heating at 310—360° being necessary for the quantitative elimination of the methyl iodide; under similar conditions cusparine does not yield methyl iodide, that due to the methoxyl group being eliminated at 200—210°.

The following new derivatives of *iso*cusparine have been prepared: *hydrobromide*, $C_{19}H_{17}O_3N,HBr,H_2O$, pale yellow leaflets, *hydrochloride*, $C_{19}H_{17}O_3N,HCl$, citron-yellow leaflets, an abnormal *aurichloride*, orange-red crystals, and *hydrogen oxalate*, $C_{19}H_{17}O_3N,H_2C_2O_4$, citron-yellow, crystalline powder.

By heating on the water-bath with nitric acid (D 1·07), *iso*cusparine is converted into a *nitro*-compound, $C_{17}H_{14}O_4N_2$, yellow or yellowish-brown crystals containing $1H_2O$, m. p. 239°, darkening at 236—237°, which contains one NMe group, forms a *hydriodide*, yellow crystals, and is isomeric with the nitro-compound, m. p. 145°, obtained from cusparine (Tröger and Runne, A., 1911, i, 482); it is also produced by heating the latter at 152—191° in the vapour of methyl iodide.

Pyrocusparine, when heated on the water-bath with nitric acid (D 1·07), is converted into a *nitro-compound*, $C_{16}H_{12}O_4N_2$, pale yellow needles, m. p. 283° (decomp.), which is also produced by demethyl-

ating the nitro-compound, m. p. 145°, by heating with hydrogen chloride. C. S.

Quinine *o*-Acetoxybenzoate. L. VANINO (*Arch. Pharm.*, 1914, **252**, 401—402).—The hydrated salt, prisms containing $3H_2O$, is prepared by mixing alcoholic solutions of *o*-acetoxybenzoic acid and hydrated quinine. The anhydrous salt, prisms, is obtained from anhydrous quinine under similar conditions (compare Santi, A., 1906, i, 977). C. S.

Physostigmine [Eserine]. II. FRITZ STRAUS (*Annalen*, 1914, **406**, 332—341. Compare A., 1914, i, 78).—Physostigmol has the composition $C_{10}H_{11}ON$, not $C_{11}H_{11}ON$ (*loc. cit.*), and therefore contains a methyl group in the place of the vinyl group. It has m. p. 103°, can be obtained in 50% yield by heating eseroline methiodide at 200° in an atmosphere of carbon dioxide, and is converted by *N*-potassium hydroxide and methyl sulphate into the *methyl ether*, $C_{11}H_{13}ON$, leaflets, m. p. 60—61°, which forms a *picrate*, red needles. The estimation of NMe in eseroline by Pregl's micro-method indicates the presence of two such groups. C. S.

Action of Acetic Anhydride on the Alkaloids of the Morphine Series. M. TIFFENEAU (*Bull. Soc. chim.*, 1914, [iv], **17**, 67—77. Compare Knorr, A., 1907, i, 789; Pschorr, A., 1907, i, 635).—In the light of the results obtained in a study of the action of acetic anhydride on tertiary benzylamines (A., 1914, i, 517), the author has examined the behaviour of various alkaloids of the morphine group towards acetic anhydride. The first part of the paper is a résumé of results published by other workers on this subject, from an examination of which the author divides this group of alkaloids into three classes according to the action of acetic anhydride on them. Morphothebaine, *apo*codeine, *apo*morphine, and its derivatives behave like tertiary benzylamines, fission occurring at the nitrogen atom. In the case of thebaine, codeinone, and *ψ*-codeinone, there is double fission at the nitrogen atom and at a carbon atom, whilst codeine, morphine, thebainone, and phenyldihydrothebaine retain their original carbon-nitrogen ring structure unchanged. These results are in accord with the recognised constitutions assigned to the various alkaloids, and support the view that the nitrogen is attached to the 9-carbon atom.

In support of his hypothesis that the action of acetic anhydride, in the cases where fission occurs, takes place in two stages, the anhydride being first added on to the tervalent nitrogen, and then fission taking place owing to the instability of the quinquevalent nitrogen, the author has shown by a series of polarimetric readings that thebaine, in the presence of acetic anhydride, shows a marked diminution in its lævo-rotation in the first twenty-four hours. At this stage the additive compound can be decomposed by water, giving the original alkaloid, but if the reaction is allowed to proceed, fission occurs.

W. G.

Action of Acetic Anhydride on the Alkaloids of the Morphine Series. II. The Morphine Bases in which Acetic Anhydride does not Produce Rupture at the Nitrogen Atom. M. TIFFENEAU (*Bull. Soc. chim.*, 1915, [iv], **17**, 109—114. Compare preceding abstract).—Diacetylmorphine, acetylcodeine, acetylcodethyline and acetylthebainone have each been heated with acetic anhydride for eight hours at 170—180°, but in every case the original base was regained unchanged, there being no rupture of the ring at the nitrogen atom. W. G.

Action of Acetic Anhydride on the Alkaloids of the Morphine Series. III. Series of *apo*Morphine; Diacetyl*apo*morphine and Triacetyl*apo*morphine. M. TIFFENEAU and PORCHER (*Bull. Soc. chim.*, 1915, [iv], **17**, 114—119. Compare preceding abstract).—By heating *apo*morphine or its hydrochloride with acetic anhydride on a water-bath for thirty hours a mixture of diacetyl- and triacetyl-*apo*morphine is obtained, and these are somewhat difficult to isolate and purify. The excess of acetic anhydride is removed by distillation on a water-bath in a vacuum. The residue is dissolved in a small amount of water containing a little acetic acid and 200—300 c.c. of water added, and the whole extracted with ether; the triacetyl*apo*morphine is thus removed. The ether extract is washed with aqueous sodium carbonate, dried over sodium sulphate, and allowed to evaporate in small portions over sulphuric acid. The aqueous solution is neutralised with sodium carbonate and immediately extracted with ether, the ethereal extract being washed with water, dried over sodium sulphate, and left to evaporate in small portions over sulphuric acid, giving crude diacetyl*apo*morphine. *Diacetyl*apo*morphine* is purified by crystallisation from a mixture of ethyl acetate and light petroleum out of contact of moist air. It yields brilliant needles, m. p. 129°, insoluble in water, soluble in most organic solvents. Its *hydrochloride* has $[\alpha]_D$ −67·26° in aqueous solution, and −47·2° in solution in acetic anhydride. The base gives a *methiodide*, m. p. 233°.

*Triacetyl*apo*morphine* is purified by crystallisation from ethyl acetate and anhydrous ether. It has m. p. 137°, and is optically inactive.

Diacetyl*apo*morphine resembles *apo*morphine in its physiological action, but triacetyl*apo*morphine does not possess any emetic properties. W. G.

Synthesis of Papaverine Derivatives of High Molecular Weight. MARTIN FREUND and KARL FLEISCHER (*Ber.*, 1915, **48**, 406—409).—Like narcotine and hydrocotarnine (A., 1912, i, 490, 491), papaverine is able to enter into condensation reactions in which the hydrogen atom at the 5-position of the *iso*quinoline group is the point of activity.

A mixture of equimolecular proportions of papaverine and opianic acid with excess of somewhat diluted sulphuric acid undergoes condensation at the ordinary temperature with formation of *opianylpapaverine*, $C_{30}H_{29}O_8N$, microscopic needles, m. p. 168—170°; *hydrochloride*, needles with $1H_2O$, decomp. when anhydrous at 167°. The

colourless solution of the base in concentrated acid on the addition of a little dilute sulphuric acid becomes violet.

In a similar manner a mixture of papaverine, aqueous formaldehyde solution and diluted sulphuric acid undergoes slow condensation at the ordinary temperature, yielding *methylenedipapaverine*,

$$CH_2\left[\begin{matrix}\cdot C_6H(OMe)_2 \\ CH:CH\cdot N\end{matrix}\!\!>C\cdot CH_2\cdot C_6H_3(OMe)_2\right]_2,$$

a colourless, crystalline powder, m. p. 204—206°; *hydrochloride*, with $2H_2O$. The colourless solution of the base in sulphuric acid gives a deep blue coloration on the addition of a trace of dilute nitric acid. The methylenepapaverine described by Königs (A., 1900, i, 189), as obtained by the interaction of papaverine and formaldehyde in the absence of any condensation agent, is quite distinct from the substance now described. D. F. T.

Alkaloids of Pareira Root. M. Scholtz and O. Koch (*Arch. Pharm.*, 1914, **252**, 513—536. Compare A., 1913, i, 87, 385).—Some colour reactions of *iso*bebeerine with alkaloidal reagents are described.

When *iso*bebeerine is heated at 160° with an excess of benzoic anhydride, the nitrogen ring is ruptured and a *dibenzoyl* derivative, $OBz\cdot C_{17}H_{16}O_2\cdot NMeBz$, pale yellow crystals, m. p. 225°, is obtained. By treatment with nitrosomethylurethane and methyl-alcoholic potassium hydroxide, *iso*bebeerine is converted into *methyl*-iso*bebeerine*, $C_{16}H_{14}O(OMe)_2{:}NMe$, amorphous, pale yellow powder, decomp. about 225°, which yields the *methiodide*,

$$C_{16}H_{14}O(OMe)_2{:}NMe,MeI,$$

colourless needles, m. p. 294°, by the action of methyl iodide in warm chloroform. The same methiodide is obtained from *iso*bebeerine by the action of methyl-alcoholic sodium methoxide and methyl iodide or of methyl sulphate and *N*-potassium hydroxide followed by that of potassium iodide. iso*Bebeerine ethiodide*, needles, m. p. 264—265° (decomp.), and *ethyl*iso*bebeerine ethiodide*, slender needles, m. p. 240°, are described.

*α-Methyl*iso*bebeerimethine*, $C_{16}H_{13}O(OMe)_2\cdot NMe_2$, colourless needles, m. p. 211°, is obtained by boiling methyl*iso*bebeerine methiodide or, much better, the methochloride with aqueous sodium hydroxide, and also by warming an aqueous solution of the methochloride with 5% sodium amalgam; the former methods also yield a by-product, *β-methyl*iso*bebeerimethine*, $C_{16}H_{13}O(OMe)_2\cdot NMe_2$, colourless needles, m. p. 185°, $[\alpha]_D^{20}+171{\cdot}4°$ in pyridine ($c=1{\cdot}4$), which develops successively greenish-yellow, cherry-red, and blue colorations with warm concentrated sulphuric acid and forms a *hydrochloride*, rhombic plates, *sulphate*, needles, and *perchlorate*, needles.

α-Methyl*iso*bebeerimethine is optically inactive, forms a colourless solution in cold, a cherry-red solution in warm, concentrated sulphuric acid, and yields a *hydrochloride*, colourless needles, decomp. 282°, *sulphate*, needles, decomp. 295—305°, *perchlorate*, decomp. about 285°, *picrate*, m. p. 202—204°, and *methiodide*, rhombic plates, m. p. above 325°, darkening above 300°. The last compound, or preferably the corresponding *methochloride*, m. p. above 310°, is decomposed into trimethylamine and a *substance*, $C_{18}H_{18}O_3$, feathery needles, m. p. 256°,

by boiling aqueous potassium hydroxide, and into trimethylamine and a *substance*, $C_{18}H_{20}O_3$, rhombic leaflets or slender needles, m. p. 325° (*dibromide*, $C_{18}H_{20}O_3Br_2$, m. p. 228—230° [decomp.]), by 5% sodium amalgam on the water-bath. By oxidation with potassium permanganate in aqueous acetone the substance $C_{18}H_{20}O_3$ yields an amorphous acid and a second product (a glycol ?), which have not been examined owing to lack of material.

The physiological action of *iso*bebeerine and of some of its derivatives has been investigated. C. S.

Vicine and Divicine. EMIL FISCHER (*Ber.*, 1914, **47**, 2611—2615). —It has been stated recently (Johnson and Johns, A., 1914, i, 579) that the divicine obtained by Ritthausen from vicine by the action of sulphuric acid is in all probability 4 : 5-diaminouracil. A sample of Ritthausen's divicine, however, does not give uric acid when heated with carbamide, which reaction can be effected quantitatively with 4 : 5-diaminouracil. The two bases are certainly very similar, but the sulphate of the former unlike that of the latter substance crystallises in an anhydrous condition, and there are other differences between the two compounds. It is possible that the subtances are geometrical isomerides, but their identity does not appear probable.

The sugar obtained by hydrolysis of vicine with dilute sulphuric acid is dextrose. D. F. T.

The Pyrrole Group. XI. The Reaction of Tertiary Pyrroles with Magnesium Compounds. BERNARDO ODDO (*Ber.*, 1914, **47**, 2427—2431).—The author has already shown that tertiary pyrroles do not react with organomagnesium haloids and that this class of reagent can be used to distinguish secondary from tertiary pyrroles; he re-affirms this view after careful experimental examination. The conflicting results of Hess and Wissing (A., 1914, i, 725) are attributed to the presence of pyrrole in their 1-methylpyrrole and to mis-interpretation of their experimental facts (compare A., 1914, i, 1142). D. F. T.

Constitution of the Colouring Matter of Blood. Hæmopyrrole and the Phonopyrrolecarboxylic Acids. O. PILOTY, J. STOCK, and E. DORMANN (*Annalen*, 1914, **406**, 342—374).—The paper is mainly a repetition of matter already recorded (A., 1909, i, 537; 1910, i, 133; 1911, i, 92; 1912, i, 519, 923; 1913, i, 539).

By reduction with hydrogen iodide in glacial acetic acid, hæmin yields, as is known, a complicated mixture of pyrrole homologues and of phonopyrrolecarboxylic acids. The latter have not been completely separated, but at least four acids (phonopyrrolecarboxylic acids *a*, *b*, *c*, and *d*) have been isolated. The mixture of pyrrole homologues (hæmopyrrole) has been separated by fractional distillation and treatment of the individual fractions with ethereal picric acid into seven bases precipitated by picric acid (hæmopyrroles *a*, *b*, *c*, *d*, *e*, *f*, *g*) and at least four bases which are not precipitated by picric acid; the method of separation gives approximately quantitative results.

Hæmopyrrole-*d* (phyllopyrrole) is now found to contain a second

tetra-substituted pyrrole derivative, which is called *haemopyrrole-g*. It has the formula $C_{10}H_{17}N$ (probably 2 : 3-dimethyl-4 : 5-diethylpyrrole), m. p. 68—69°, b. p. 91·5—93°/10·5 mm., forms a *picrate*, m. p. 105·5°, and does not exhibit the pine-shaving reaction. Hæmopyrrole-*d*, after the removal of hæmopyrrole-*g*, has m. p. 69°, and its picrate has m. p. 104—105°; for the unpurified hæmopyrrole-*d* (phyllopyrrole) and its picrate, Willstätter and Asahina give m. p. 60—62° and 95° respectively.

From phonopyrrolecarboxylic acid-*a* the authors have obtained hæmopyrrole-*b* in the form of its picrate. Since the latter has been proved by synthesis to be 2 : 3-dimethyl-4-ethylpyrrole (Piloty and Blömer, A., 1913, i, 196), phonopyrrolecarboxylic acid-*a* must be 2 : 3-dimethylpyrrole-4-β-propionic acid,

$$\begin{matrix} CMe{:}CMe \\ | \\ NH{-}{-}{-}CH \end{matrix}\!\!>\!C\cdot CH_2\cdot CH_2\cdot CO_2H.$$

Consequently, phonopyrrolecarboxylic acid-*b* (*iso*phonopyrrolecarboxylic acid) must be 2 : 5-dimethylpyrrole-4-β-propionic acid, since its oxime is isomeric with that of phonopyrrolecarboxylic acid-*a*, and both oximes yield the same hæmatic acid. Phonopyrrolecarboxylic acid-*c* (xanthopyrrolecarboxylic acid) is most probably 3-methyl-5-ethylpyrrole-4-β-propionic acid, since it yields the same oxime and the same hæmatic acid as phonopyrrolecarboxylic acid-*b*. Finally, phonopyrrolecarboxylic acid-*d*, which is isomeric with the *c*-acid, does not form an oxime; consequently, it contains substituents in the two α-positions and is most probably 2 : 3 : 5-trimethylpyrrole-4-β-propionic acid.

Hæmopyrrole-*e* cannot be 2 : 3-dimethyl-1-ethylpyrrole as previously suggested (A., 1912, i, 923), because this pyrrole derivative has been synthesised by Piloty and Wilke (A., 1913, i, 767), and does not yield a picrate corresponding with that of hæmopyrrole-*e*.

The authors advance some speculations as to the constitution of hæmin. C. S.

A New Method for the Preparation of Pyrrole-2-aldehyde. V. V. Tschelincev and A. Terentjev (*Ber.*, 1914, **47**, 2652—2654; also *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1405—1409. Compare this vol., i, 470).—The method described for the preparation of acylpyrroles from magnesium pyrryl bromide and an aliphatic ester can be extended to ethyl formate, in which case the product is the corresponding formyl derivative or pyrrole-2-aldehyde. Propyl and *iso*amyl formates give the same result. As there was in all cases a tendency to form resins with diminution in the yield of aldehyde, it was found that a better yield could be obtained by dispensing with ether and preparing the original organomagnesium compound as a suspension in benzene; this was then successively treated with pyrrole and the alkyl formate.

The resulting pyrrole-2-aldehyde, m. p. 45°, b. p. 217—219°, gives a *semicarbazone*, rhombic crystals or leaflets, m. p. 183·5°. D. F. T.

Preparation of Pyrrolealdehyde. L. Alessandri (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 65—70).—Pyrrole-2-aldehyde (Bamberger and Djierdijan, A., 1900, i, 309) can be prepared also by the

action of *iso*amyl formate on pyrrole in the presence of sodium, and by the action of *iso*amyl formate on magnesium pyrryl iodide. A convenient means of identification is found in the preparation of the *azine*, $C_{10}H_{10}N_4$, by means of a slightly alkaline solution of hydrazine sulphate; it forms small, yellow needles, m. p. 170° (with slight decomposition). R. V. S.

Internally Complex Salts. XIII. Residual Affinity of Internally Complex Salts. H. Ley (*Ber.*, 1914, **47**, 2948—2956).—The power of internally complex salts to form additive compounds with ammonia has been studied, in order to obtain some idea of the residual affinity of such substances.

The additive power is found to vary enormously. The cupric salts of piperidineacetic and cinchonic acids behave like normal salts and combine with 4—6 molecular proportions of ammonia; under similar conditions, copper aminoacetate combines with two mols., whereas the piperidineacetate absorbs five mols.; the copper hydroxyamidines (this vol., i, 459, 464) and many other complex salts do not combine with ammonia at all. In order to explain these differences, it is necessary to consider, not only the number, but the "strength" of the auxiliary valencies. The total "strength" of the unions by main valencies and auxiliary valencies is constant for any metal, so that if this amounts to the maximum value in a given compound (as in the above internal complexes) there is no tendency to further combination, that is, the compound is "saturated." The extreme cases are those of compounds like mercury diphenyl in which the union by main valencies absorbs practically the whole of the affinity, and of complexes like $[M(NH_3)_6]X_n$, in which the greater part of the affinity is satisfied by auxiliary valencies. As a rule, however, internally complex salts display a certain amount of residual affinity.

Anhydrous copper piperidineacetate forms a *pentammine* at ordinary temperatures; cupriacetylacetone forms a pale green *diammine* at ordinary temperatures and a deep blue *pentammine* at $-20°$, whereas nickelo- and cobalto-acetylacetone form more stable diammines and cobaltiacetylacetone does not absorb ammonia at all; cupribenzoylacetone forms a greenish-yellow *diammine* and at $-20°$ a blue *hexammine*; ethyl cupriacetoacetate forms a green *diammine*; and copper cinchonate yields a blue *hexammine*.

In order to obtain a rough idea of the "strength" of the auxiliary valencies with which ammonia is attached in such compounds, the vapour pressure above them may be measured. It might be expected that the introduction of an amino-group, X, into an anion, R, would make such a demand on the affinity of the metal that the ammonia of the ammine, for example, $M(RX)_2,2NH_3$, would be more loosely held than in the case of the unsubstituted compound, $MR_2,2NH_3$. Experiments are described which show that this is the case, for the partial pressure above copper aminoacetate diammine,

$$Cu(CO_2\cdot CH_2\cdot NH_2)_2,2NH_3,$$

is about 500 mm. at 25°, but above copper acetate diammine,

$$Cu(CO_2Me)_2,2NH_3,$$

it is too small to be measured. J. C. W.

Compounds of Pyridine and Picoline with Metallic Sodium. BRUNO EMMERT (*Ber.*, 1914, **47**, 2598—2601).—It has already been observed by several workers that the action of sodium on pyridine, picoline or quinoline gives rise to dark-coloured masses which under the influence of atmospheric moisture regenerate the original bases together with dipyridyl, dipicolyl, and diquinolyl respectively and even hydrogenation products of dipyridyl in the case of the first base. The sodium compounds have, however, not been described.

Sodium rapidly attacks pyridine in an atmosphere of nitrogen at the ordinary temperature, and after one or two days the metal has completely disappeared, but no evolution of gas is observable. If the pyridine is present in the proportion of two molecules to an atom of the metal, the product is quite dry and homogeneous; other proportions give a residual excess of one or other of the reagents. These results together with those of analysis indicate a composition $(C_5H_5N)_2Na$, the existence of which has a rough parallel in the compound $(NH_3)_5Na$ (Ruff and Zedner, A., 1908, ii, 585).

α-Picoline exhibits similar behaviour to pyridine, giving a *compound*, $(C_6H_7N)_2Na$. D. F. T.

Some Aldehydic Compounds. A. ANGELI and LUIGI ALESSANDRI (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 93—106).—1 : 2-Dimethylindole-3-aldehyde, $NMe\langle\begin{matrix}C_6H_4\\CMe\end{matrix}\rangle C\cdot CHO$, is obtained by boiling equimolecular quantities of Plancher and Ponti's aldehyde (A., 1907, i, 341) and methyl iodide with sodium in methyl alcohol; it forms rhomboidal crystals, m. p. 129°. It yields a *phenylhydrazone*, $C_{17}H_{17}N_3$, which crystallises in silky needles, m. p. 154° (decomp.). The *oxime*, $C_{11}H_{12}ON_2$, forms needles, m. p. 171°. With semicarbazide it yields a *substance* crystallising in needles which turn yellow at about 210° and decompose at 265—267°.

2-Methylindole-3-aldehyde (Plancher and Ponti, *loc. cit.*) gives an *oxime*, $C_{10}H_{10}ON_2$, which forms needles, m. p. 153°. This aldehyde yields a *sodium* salt, but no salt could be obtained from 1 : 2-dimethylindole-3-aldehyde.

2-Methylindole-3-aldehyde gives acetylanthranilic acid on oxidation with permanganate, showing that it reacts chiefly in the hydroxymethylene form, but 1 : 2-dimethylindole-3-aldehyde in similar circumstances yields 1 : 2-dimethylindole-3-carboxylic acid almost quantitatively.

Pyrrole-2-aldehyde was regarded by Bamberger as an aldehyde, although its behaviour is anomalous in many respects. The authors consider that it has a hydroxymethylenic structure

$$CH\langle\begin{matrix}CH:CH\\N\text{------}\end{matrix}\rangle C{:}CH\cdot OH,$$

which represents its reactions better. It forms a sodium salt.

The 1-methylpyrrole-2-aldehyde recently described (E. Fischer, A., 1913, i, 1225) behaves differently because it has no mobile hydrogen atom. Whilst pyrrole-2-aldehyde does not react with benzenesulphhydroxamic acid, the methylated aldehyde does react with

this substance, yielding an hydroxamic acid, which shows with ferric chloride a red coloration which passes into blue. Owing to the small quantity of substance available, the acid could not be isolated when prepared in this way, but *2-pyrrolehydroxamic acid* prepared from pyrrole-2-carboxylic acid and hydroxylamine in the presence of sodium ethoxide shows the same colour reaction; the acid forms prisms tinged with red, m. p. 112—113° (decomp.).

When equimolecular quantities of hydroxylamine, methyl benzilate and sodium are kept in alcohol for twenty-four hours, *benzilhydroxamic acid*, $C_{14}H_{13}O_3N$, is obtained; it forms colourless needles decomposing at 139°. *Mandelhydroxamic acid*, $C_8H_9O_3N$ (from ethyl mandelate), forms lustrous plates, m. p. 147° (decomp.). Its *copper* salt has the composition $C_8H_7O_3NCu$. These two acids resemble that which can be obtained from glyceraldehyde; they give the same wine-red coloration with ferric chloride and an intense violet coloration with a trace of copper in presence of alkali. On heating, benzilhydroxamic acid yields benzophenone as well as ammonia and carbon dioxide, whilst from mandelhydroxamic acid, benzaldehyde is formed.

R. V. S.

Colourless Additive Products of Quinoline and Pyridine with Fluorescein. Bernardo Oddo (*Ber.*, 1914, **47**, 2433. Compare A., 1913, i, 1110; Oddo and Vassallo, A., 1912, i, 792).—A reply to Fischer and Hoffmann (A., 1914, i, 866). D. F. T.

Dinitro-α-naphthylpyridinium Chloride and its Transformation Products. Th. Zincke and Fr. Krollpfeiffer (*Annalen*, 1915, **408**, 285—314).—*2 : 4-Dinitro-α-naphthylpyridinium chloride*, $C_5H_5NCl\cdot C_{10}H_5(NO_2)_2$, colourless crystals, m. p. about 140° (decomp.), is obtained by boiling a suspension of 1-chloro-2 : 4-dinitronaphthalene in alcohol and pyridine. It is easily decomposed into its components, for example, by fusion or by evaporation with dilute hydrochloric acid. In aqueous solution, it suffers very little hydrolytic change, yielding 2 : 4-dinitro-α-naphthol and pyridine; the hydrolysis is accelerated by sodium nitrite or acetate. Pyridine in the presence of alcohol produces hydrolysis, so that in its preparation the dinitronaphthylpyridinium chloride is always accompanied by *dinitro-α-naphthylpyridinium 2 : 4-dinitro-α-naphthyl oxide*, $C_{10}H_5(NO_2)_2\cdot C_5NH_5\cdot O\cdot C_{10}H_5(NO_2)_2$, red leaflets or needles, m. p. about 210° (decomp.).

By treatment with aqueous alkali hydroxide, sodium carbonate, or ammonia, or, best, with 5% alcoholic sodium ethoxide, 2 : 4-dinitro-α-naphthylpyridinium chloride yields a deep bluish-violet precipitate which on immediate acidification is converted into a *substance*, $C_{15}H_{11}O_5N_3$, dark red prisms with a metallic lustre, decomp. about 190°. This substance is quite analogous to that obtained from dinitrophenylpyridinium chloride (Zincke, A., 1904, i, 448; 1905, i, 467) and therefore probably has the constitution

$C_{10}H_5(NO_2)_2\cdot N{:}CH\cdot CH{:}CH\cdot CH{:}CH\cdot OH$ or

$C_{10}H_5(NO_2)_2\cdot NH\cdot CH{:}CH\cdot CH{:}CH\cdot CHO$. It reacts in accordance with both formulæ and forms an *acetate*, yellow, crystalline powder,

m. p. 166—167° (decomp.), *benzoate*, yellow powder, m. p. 170—180° (decomp.), *ethyl carbonato*-derivative, citron-yellow prisms, m. p. about 180° (decomp.), *phenylhydrazone*, black, crystalline powder, m. p. about 140° (decomp.), and *oxime*, brownish-red scales with a metallic green lustre, m. p. 166—167° (decomp.). All these derivatives are decomposed by hydrochloric acid, yielding 2 : 4-dinitro-α-naphthylamine; the other product, the aldehyde-alcohol, could not be isolated.

The action of alcoholic ammonia on 2 : 4-dinitro-α-naphthylpyridinium chloride is quite different from that of an aqueous solution, and results in the formation of an *amine*, $C_{15}H_{12}O_4N_4$, brownish-violet, crystalline powder with a bronze lustre, m. p. 143—145° (decomp.); similarly, methylamine and dimethylamine respectively yield a *methylamine* derivative, $C_{16}H_{14}O_4N_4$, blackish-green crystals, m. p. about 123—125° (decomp.) (*hydrochloride*, red needles), and a *dimethylamine* derivative, $C_{17}H_{16}O_4N_4$, black scales with metallic green lustre, m. p. about 178—180° (decomp.) (*hydrochloride*, dark red scales with metallic green lustre). The amine, which probably has the constitution

$$C_{10}H_5(NO_2)_2\cdot N{:}CH\cdot CH{:}CH\cdot CH{:}CH\cdot NH_2,$$

forms a *hydrochloride*, orange-gold leaflets, *platinichloride*, red crystals, and *nitrate*, red, crystalline powder, yields 2 : 4-dinitro-α-naphthylamine, pyridine, and ammonia by heating with alcohol and hydrochloric acid, and 2 : 4-dinitro-α-naphthol or its derivatives by heating with organic acids or their anhydrides, and is converted, by loss of ammonia, into an *imine*, $NH(C_{15}H_{10}O_4N_3)_2$, black, crystalline powder or dark brown scales, m. p. about 195—200° (decomp.), by solution in glacial acetic acid or, better, by boiling with benzene.

The red alkali product mentioned above regenerates 2 : 4-dinitro-α-naphthylpyridinium chloride by treatment with hydrogen chloride in glacial acetic acid and is converted by prolonged contact with acetone into a yellow *isomeride*, $C_{15}H_{11}O_5N_3$, m. p. about 190° (decomp.), which is less reactive than, and has not reconverted into, the red substance; the same yellow isomeride appears to be formed by the action of methyl, ethyl, or *iso*butyl alcohol.

2 : 4-Dinitro-α-naphthylpyridinium chloride reacts with hydrogen sulphide in aqueous solution to form 2 : 4-*dinitro-α-naphthyl mercaptan*, $C_{10}H_5(NO_2)_2\cdot SH$, yellow powder, m. p. 117—118° (decomp.), and the *disulphide*, $S_2[C_{10}H_5(NO_2)_2]_2$, brownish-red powder, m. p. about 145° (decomp.), in alcoholic solution to form the *sulphide*, $S[C_{10}H_5(NO_2)_2]_2$, yellow needles, m. p. 273—274° (decomp.). C. S.

Dinitro-α-naphthyl*iso*quinolinium Chloride and its Transformation Products. Th. Zincke and Fr. Krollpfeiffer (*Annalen*, 1915, **408**, 314—339. Compare preceding abstract).—1-Chloro-2 : 4-dinitronaphthalene does not react with quinoline, but with *iso*quinoline in boiling alcohol readily yields 2-2′ : 4′-*dinitro-α-naphthyliso-quinolinium chloride*, $C_9H_7NCl\cdot C_{10}H_5(NO_2)_2$, stout prisms or tufts of needles, m. p. 160—165° (decomp.). The corresponding *nitrate*, colourless needles, has m. p. 170° (decomp.).

Dinitro-α-naphthyl*iso*quinolinium chloride resembles dinitro-α-naphthylpyridinium chloride (*loc. cit.*) in its behaviour on heating, hydrolysis in aqueous solution, and reaction with hydrogen sulphide, but its

transformation by alkalis, sodium carbonate, or ammonia is very different, a *ψ-base*, $C_6H_4<\begin{matrix}CH{=}CH\\CH(OH)\end{matrix}>N\cdot C_{10}H_5(NO_2)_2$, dark brown, amorphous powder, m. p. 165—200° (decomp.), being produced; in this respect it resembles 2-*op*-dinitrophenyl*iso*quinolinium chloride (Zincke and Weisspfenning, A., 1913, i, 389). The *ψ*-base, which is also obtained from the chloride by the action of alkyl- or aryl-amines in the presence of water, is converted into salts of dinitro-*α*-naphthyl-*iso*quinolinium hydroxide by dilute acid, even by acetic acid, and is converted into ethers, $C_6H_4<\begin{matrix}CH{=}CH\\CH(OR)\end{matrix}>N\cdot C_{10}H_5(NO_2)_2$, by boiling with alcohols; the *methyl ether*, dark red needles, m. p. 160° (decomp.), *ethyl ether*, brownish-violet leaflets, m. p. 150° (decomp.), and iso*butyl ether*, almost black crystals, m. p. 118° (decomp.), have been prepared and each can be converted into the others by boiling with the necessary alcohol.

When the *ψ*-base is dissolved in dilute hydrochloric acid, there is formed, in addition to dinitronaphthyl*iso*quinolinium chloride, a small amount of the *hydrochloride* of an anhydro-base (which cannot be isolated), $C_{38}H_{25}O_9N_6Cl$, red powder, m. p. 110° (decomp.). This salt, which is also produced from the *ψ*-base and dinitronaphthyl*iso*quinolinium chloride in methyl-alcoholic solution, is converted into the *ψ*-base by alkalis and into dinitro-*α*-naphthyl*iso*quinolinium chloride by concentrated hydrochloric acid.

The action of various amines on dinitro-*α*-naphthyl*iso*quinolinium chloride, the *ψ*-base, and its ethers is different under different conditions. Aniline and *p*-toluidine convert the chloride into the *ψ*-base in aqueous solution, but into *iso*quinoline and phenyl-dinitro-*α*-naphthylamine and p-*tolyl*-2 : 4-*dinitro-α-naphthylamine*, orange-yellow needles, m. p. 201°, in alcoholic solution or without a solvent; the same two amines convert the *ψ*-base or its ethers in boiling alcohol into 2 : 4-dinitro-*α*-naphthylamine and phenyl- or *p*-tolyl-*iso*quinolinium compounds (compare Zincke and Weisspfenning, *loc. cit.*). Methyl- or ethyl-amine converts dinitro-*α*-naphthyl*iso*-quinolinium chloride or the *ψ*-base in boiling alcohol into 2 : 4-dinitro-*α*-naphthylamine and an alkyl*iso*quinolinium chloride. An alcoholic solution containing a small quantity of dimethylamine converts dinitro-*α*-naphthyl*iso*quinolinium chloride into the methyl ether of the *ψ*-base, but with an excess of dimethylamine a *ψ*-ammonium base, 1-*dimethylamino*-2-2′ : 4′-*dinitro-α-naphthyl*-1 : 2-*dihydro*isoquinoline,

$$C_6H_4<\begin{matrix}CH{:}CH\\CH(NMe_2)\end{matrix}>N\cdot C_{10}H_5(NO_2)_2,$$

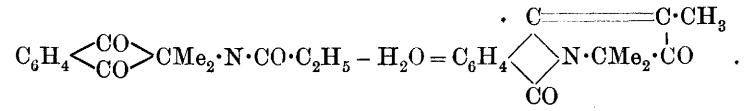
dark bluish scales, m. p. 155° (decomp.), is obtained. This base, which is also obtained from the dinitronaphthyl*iso*quinolinium chloride and dimethylamine in benzene (ammonia under these conditions produces an *imine*, $NH[C_9H_7N\cdot C_{10}H_5(NO_2)_2]$, black powder), regenerates the *iso*quinolinium salt by treatment with dilute acids, yields ethers of the *ψ*-(carbinol) base by boiling with alcohols, and is hydrolysed by an excess of dimethylamine in boiling alcohol, being converted into 2 : 4-dinitro-*α*-naphthylamine and presumably an aldehyde-alcohol; the latter, however, could not be isolated, although

from the solution a p-*nitrophenylhydrazone*, red, apparently crystalline substance, m. p. 185—190° (decomp.), was obtained in small quantity.

Dinitro-α-naphthyl*iso*quinolinium chloride or the ψ-(carbinol) base in alcoholic solution is converted by phenylhydrazine into a *phenylhydrazone*, $C_{10}H_5(NO_2)_2\cdot NH\cdot CH{:}CH\cdot C_6H_4\cdot CH{:}N\cdot NHPh$, brownish-red scales with a golden lustre, m. p. about 145° (decomp.), which is converted by alcoholic hydrogen chloride into 2 : 4-dinitro-α-naphthylamine and anilino*iso*quinolinium chloride (Zincke and Weisspfenning, *loc. cit.*). The red substance obtained from the latter by the action of 2*N*-sodium carbonate (*loc. cit.*) is converted by moderately concentrated aqueous potassium cyanide into the *nitrile*, m. p. 93°, colourless needles, of *iso*quinoline-1-carboxylic acid. *Anilino*iso*quinolinium ψ-cyanide*, $C_6H_4<\begin{matrix}CH=CH\\CH(CN)\end{matrix}>N\cdot NHPh$, almost colourless needles, m. p. 110°, which is doubtless formed but cannot be isolated in the preceding reaction, is obtained from anilino*iso*quinolinium chloride and potassium cyanide in aqueous solution, and is converted into aniline and the preceding nitrile by methyl-alcoholic sodium methoxide or potassium cyanide. C. S.

Preparation of Nitrogenous Condensation Products [Dyes] of the Anthraquinone Series. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 280190; from *J. Soc. Chem. Ind.*, 1915, **34**, 348. Compare this vol., i, 21).—*N*-Aryl-α-anthrapyrrolecarboxylic acids are formed when esters of the α-anthraquinonylarylglycines are heated in neutral solvents, under atmospheric or increased pressure, with alkali or alkaline earth hydroxides. They are yellow to brown substances which dye wool yellow to blue shades in an acetic acid-acetate bath. J. C. W.

Action of Acylamino-acid Chlorides on Ethyl Sodiomalonate. III. S. GABRIEL (*Ber.*, 1914, **47**, 2922—2925. Compare A., 1913, i, 622).—An improved process for the preparation of phthaliminomethylpentanone, $C_8H_4O_2N\cdot CMe_2\cdot COEt$, involves the use of aminomethylpentanone hydrochloride instead of the free amine. This salt is prepared by the decomposition with hydrochloric acid of ethyl phthaliminoisobutyrylmethylmalonate, m. p. 121°. At 210° it combines with an equimolecular proportion of phthalic anhydride to form the pentanone, m. p. 70°, which is converted by sodium methoxide into *benzoylenetrimethylpyrrolone*, crystals, m. p. 204—205° (with production of an intense yellow coloration):



The process for the preparation of phenyltrimethylpyrrolone has been modified by the isolation of methylaminoisobutyronitrile, benzoylation of the product, and hydrolysis of the cyano-group. *α-Methylaminoisobutyronitrile* boils at 63—65°/28 mm., and forms a *platinichloride*, long, very soluble needles. Benzoyl chloride converts the nitrile into *trimethylhippuronitrile*, prisms, m. p. 120°, which is

hydrolysed by concentrated sulphuric acid to the corresponding *trimethylhippuric acid*, $C_6H_5\cdot CO\cdot NMe\cdot CMe_2\cdot CO_2H$, m. p. 183°.

On reduction with sodium amalgam, phenyltrimethylpyrrolone is converted into *phenyltrimethylpyrrolidone*, $C_6H_5\cdot CH<\begin{matrix}CH_2-CO\\ |\\ NMe\cdot CMe_2\end{matrix}$, quadratic prisms, m. p. 70—71°, b. p. 274—275°/762 mm. This substance forms a *platinichloride*, pointed needles, m. p. 235°; a *picrate*, m. p. 201°; an *aurichloride*, m. p. 164—166° (decomp.); and a *phenylhydrazone*, needles, m. p. 151°. A. J. W.

Inner Complex Salts. XI. Salt Formation by Hydroxylamidoximes. H. Ley and M. Ulrich (*Ber.*, 1914, **47**, 2938—2944). —The formula $\overset{\alpha}{O}H\cdot N:\overset{\beta}{C}\cdot\overset{\gamma}{N}\cdot\overset{\delta}{O}H$ is proposed to represent the nucleus of the substituted hydroxylamidoximes. The *cupric* salt of *acetohydroxylamidoxime* is formed from acetohydroximyl chloride, hydroxylamine, and copper acetate. The analogous *cupric* salt of *benzohydroxylamid oxime* is reddish-brown. Reduction of benzohydroxylamidoxime by sulphurous acid yields benzamidoxime. m-*Nitrobenzohydroxylamidoxime*, from *m*-nitrobenzohydroximyl chloride and hydroxylamine, forms light yellow crystals, m. p. 118—119°. Its *hydrochloride* has m. p. 158° (decomp.), its *copper* salt is a sepia-brown, crystalline mass, and its *nickel* salt forms green crystals, turning blue. Reduction of the oxime with sulphurous acid yields *m*-nitrobenzenylamidoxime, m. p. 172°.

β-Phenyl-γ benzylhydroxylamidoxime forms white needles, m. p. 112—113°, and gives a deep-blue coloration with ferric chloride. Its *cupric* salt forms reddish-brown crystals, m. p. 133—135° (decomp.). The *nickel* salt is brownish-green, and the *cobalt* salt similar. The *hydrochloride* forms white crystals, m. p. 170°.

β-Phenyl-δ-benzyloxyamidoxime forms white needles, m. p. 109—110°, and gives a deep blue coloration with ferric chloride. Its *cupric* salt is a dark brown, amorphous substance. The *nickel* salt is green in solution, and the cobalt salt brown. They have not been isolated. A. J. W.

The Action of Hydrazobenzene on Some Organic Acids and Acid Anhydrides. Ernst Simonyi (*Ber.*, 1914, **47**, 2657—2663). —When phthalic anhydride and hydrazobenzene are heated together in a sealed tube at 200°, *diphthalylbenzidine*,

$$C_6H_4<\begin{matrix}CO\\ CO\end{matrix}>N\cdot C_6H_4\cdot C_6H_4\cdot N<\begin{matrix}CO\\ CO\end{matrix}>C_6H_4,$$

yellow crystals, m. p. above 360°, is obtained; *tetrabromo*-derivative, $C_{12}H_4Br_4\left(N<\begin{matrix}CO\\ CO\end{matrix}>C_6H_4\right)_2$, m. p. above 340°; *dinitro*-derivative,

$$C_{12}H_6(NO_2)_2\left(N<\begin{matrix}CO\\ CO\end{matrix}>C_6H_4\right)_2,$$

yellow needles, m. p. 240°. Heating with phosphorus pentachloride for five hours at 250° converted the substance into the chloro-*compound*, $C_{12}H_8\left(N<\begin{matrix}CCl_2\\ CCl_2\end{matrix}>C_6H_4\right)_2$, yellow crystals, m. p. above 350°.

Succinic anhydride and hydrazobenzene react at 180°, giving *disuccinylbenzidine*, $C_{12}H_8\left(N<\begin{matrix}CO\cdot CH_2\\ |\\ CO\cdot CH_2\end{matrix}\right)_2$, needles, m. p. 335°; *dinitro*-derivative, $C_{12}H_6(NO_2)_2\left(N<\begin{matrix}CO\cdot CH_2\\ |\\ CO\cdot CH_2\end{matrix}\right)_2$, orange-yellow crystals, m. p. 140°; *tetrabromo*-derivative, $C_{12}H_4Br_4\left(N<\begin{matrix}CO\cdot CH_2\\ |\\ CO\cdot CH_2\end{matrix}\right)_2$, reddish-brown crystals, m. p. 375°. The action of phosphorus pentachloride converts the compound into a *substance*, $C_{12}H_8\left(N<\begin{matrix}CCl_2\cdot CH_2\\ |\\ CCl_2\cdot CH_2\end{matrix}\right)_2$, yellow crystals, m. p. 162°.

Under similar conditions, benzoic anhydride and hydrazobenzene yielded *dibenzoyldiphenylhydrazine*, NPhBz·NPhBz, yellow crystals, m. p. 55°; *dinitro*-derivative, $N_2Bz_2(C_6H_4\cdot NO_2)_2$, brownish-red crystals, m. p. 140°. Phosphorus pentachloride at 138° produced a *tetrachloro*-compound, $N_2Ph_2(CCl_2Ph)_2$, olive-coloured crystals, m. p. 85°. Condensation of benzidine and benzoic anhydride at 250° gave a colourless, crystalline *substance*, m. p. 352°. D. F. T.

Polymerisation with Tri- and Tetra-alkylated Pyrroles. HANS FISCHER (*Ber.*, 1915, **48**, 401—406).—Although pyrrole condenses readily to tripyrrole and 2 : 3-dialkylpyrroles are known to polymerise to di-pyrrole derivatives, no definite case of similar condensation of tri-substituted pyrroles has been described. It has now been found that 2 : 4-dimethyl-3-ethylpyrrole (cryptopyrrole) under the action of hydrogen chloride on its ethereal solution gives a deposit of the *hydrochloride* of a *dicryptopyrrole*; a similar polymerisation occurs when the picrate of 2 : 4-dimethyl-3-ethylpyrrole is boiled with ethyl acetate for two hours; the orange-red *picrate*, which fails to give the Ehrlich reaction, has m. p. 154·5° (corr.), and on treatment with sodium hydroxide solution gives the free dipolymeride, presumably of the structure $CMe<\begin{matrix}CEt\cdot CMe\cdot CMe\cdot CEt\\ |\quad\quad\quad\quad\quad |\\ NH\cdot CH\text{--}CH\cdot NH\end{matrix}>CMe$, as an oil. Cryptopyrrole can be re-obtained from the polymeride by heating to a temperature above 200° in a vacuum.

2 : 4 : 5-Trimethyl-3-ethylpyrrole (phyllopyrrole) polymerises more readily, and on heating the picrate with ethyl acetate for a half-hour there is obtained the yellow *picrate*, m. p. 147·5° (corr.) of the *dimeride*, which can be liberated as an oil by sodium hydroxide solution. The oil can be de-polymerised by distillation with steam or heating in a vacuum to 150°. In the light of these results, hæmopyrrole-*e* (Piloty and others, A., 1912, i, 923; 1913, i, 767) is to be regarded as polymerised cryptopyrrole, hæmopyrrole-*g* as an impure phyllopyrrole, and hæmopyrrole-*f* as another dimeride of this class.

The methylation of phonopyrrolecarboxylic acid to trimethylpyrrole-propionic acid (phyllopyrrolecarboxylic acid) by sodium methoxide as described by Fischer and Bartholomäus (A., 1913, i, 209), and questioned by Piloty, Stock, and Dormann (following abstract) has been repeated, but potassium methoxide is found to give a still better result. D. F. T.

The Constitution of the Colouring Matter of Blood. Coloured Dipyrrylmethene (Dipyrrylmethane) Derivatives. III. O. PILOTY, W. KRANNICH, and H. WILL (*Ber.*, 1914, **47**, 2531—2545. Compare Piloty, Stock and Dormann, A., 1914, i, 327, 755).—The earlier portion of the paper is devoted to a claim against Fischer and Eismayer (A., 1914, i, 993) for priority. The experimental portion describes an investigation of the mode of action of chloroform and alkali on pyrrole compounds, by the interaction of which substances dipyrrylmethane derivatives are obtainable.

2 : 5-Dimethylpyrrole in chloroform solution readily reacts with aqueous potassium hydroxide solution producing *di*-3-(2 : 5-*dimethylpyrryl*)*methane*, $\begin{matrix}\mathrm{CMe{:}CH}\\ \mathrm{NH{\cdot}CMe}\end{matrix}\!\!>\!\mathrm{C{\cdot}CH{:}C}\!<\!\begin{matrix}\mathrm{CH{=}CMe}\\ \mathrm{CMe{:}N}\end{matrix}$, which was isolated as the *hydrochloride*, orange-red needles, and as the *perchlorate*. Several intermediate products were also separated, of which the most important was 2 : 5-dimethylpyrrole-3-aldehyde, $\begin{matrix}\mathrm{CMe{:}CH}\\ \mathrm{NH{\cdot}CMe}\end{matrix}\!\!>\!\mathrm{C{\cdot}CHO}$, colourless leaflets, m. p. 141°, which when moistened with concentrated hydrochloric acid underwent change with evolution of heat, giving an unstable *substance*, m. p. 60°; attempts to recrystallise this solid reconverted it into the original aldehyde. The other intermediate products included a *substance*, $C_{14}H_{20}N_2Cl_2$, prisms, m. p. 177°, which was not examined more closely, and an aromatic oily *substance*.

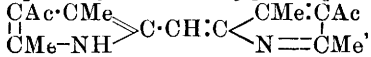
2 : 5-Dimethylpyrrole-3-aldehyde condenses with 2 : 4-dimethylpyrrole in the presence of hydrochloric acid, giving a 2 : 4-*dimethylpyrryl*-3[-2′ : 5′-*dimethylpyrryl*]-*methane*, $\begin{matrix}\mathrm{CMe{:}CH}\\ \mathrm{NH{\cdot}CMe}\end{matrix}\!\!>\!\mathrm{C{\cdot}CH{:}C}\!<\!\begin{matrix}\mathrm{CMe{:}CH}\\ \mathrm{CMe{:}N}\end{matrix}$ or $\begin{matrix}\mathrm{CMe{:}CH}\\ \mathrm{NH{\cdot}CMe}\end{matrix}\!\!>\!\mathrm{C{\cdot}CH{:}C}\!<\!\begin{matrix}\mathrm{N{=}CMe}\\ \mathrm{CMe{:}CH}\end{matrix}$, which was separated as the *perchlorate*, needles with a bronze lustre, m. p. 250° (decomp.). Condensation of 2 : 5-dimethylpyrrole-3-aldehyde with 3-acetyl-2 : 4-dimethylpyrrole under similar conditions to the preceding produces a substance which is in all probability 3-*acetyl*-2 : 4-*dimethylpyrryl*-2′ : 5′-*dimethylpyrrylmethane*, $\begin{matrix}\mathrm{CMe{:}CH}\\ \mathrm{NH{\cdot}CMe}\end{matrix}\!\!>\!\mathrm{C{\cdot}CH{:}C}\!<\!\begin{matrix}\mathrm{N{=}CMe}\\ \mathrm{CMe{:}CAc}\end{matrix}$, which was separated as the *perchlorate*, stout, red needles, m. p. 206°. In a similar manner, 2 : 5-dimethylpyrrole-3-aldehyde and ethyl 2 : 4-dimethylpyrrole-3-carboxylate undergo condensation with formation of *ethyl* 2′ : 5′-*dimethylpyrryl*-2 : 4-*dimethylpyrrylmethane*-3-*carboxylate*, $\begin{matrix}\mathrm{CMe{:}CH}\\ \mathrm{NH{\cdot}CMe}\end{matrix}\!\!>\!\mathrm{C{\cdot}CH{:}C}\!<\!\begin{matrix}\mathrm{N{=}CMe_2}\\ \mathrm{CMe{:}C{\cdot}CO_2Et}\end{matrix}$, isolated as the *hydrochloride*, orange-red needles, m. p. 182°.

3-Acetyl-2 : 4-dimethylpyrrole, when treated with chloroform and potassium hydroxide solution, gives an intermediate formation of a substance, probably *di* 5[-3-*acetyl*-2 : 4-*dimethylpyrryl*]-*carbinol*,

$$\begin{matrix}\mathrm{CAc{\cdot}CMe}\\ \mathrm{CMe{-}NH}\end{matrix}\!\!>\!\mathrm{C{\cdot}CH(OH){\cdot}C}\!<\!\begin{matrix}\mathrm{CMe{\cdot}CAc}\\ \mathrm{NH{-}CMe'}\end{matrix}$$

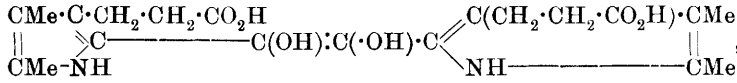
prisms, m. p. indistinct at 265°, which is rapidly converted by hydro-

chloric acid into *di*-5[-3-*acetyl*-2:4-*dimethylpyrryl*]-*methane*,

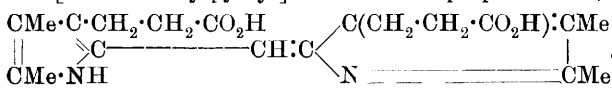


brown, hexagonal, prismatic leaflets with a green sheen, m. p. 219°; *hydrochloride*, orange prisms with blue sheen, m. p. 199° (decomp.).

In alcoholic solution at 40°, phonopyrrolecarboxylic acid undergoes condensation with glyoxal, giving brownish-red, prismatic leaflets of a *substance*,



m. p. 217°; *acetate*, needles, m. p. 224°; *hydrochloride*, prismatic crystals with green lustre. There is produced at the same time in the condensation di[2 : 3-dimethylpyrryl]-methane-di-4-propionic acid,



m. p. 240°, which has already been described (A., 1914, i, 327).

Condensation of ethyl 2 : 4-dimethylpyrrolecarboxylate with formaldehyde in aqueous alcoholic solution in the presence of hydrochloric acid gives rise to the *compound*, $C_{19}H_{26}O_4N_2$, almost colourless prisms, m. p. 223·5°, which readily undergoes oxidation by ferric chloride in alcoholic solution with formation of the hydrochloride (red needles with blue lustre, m. p. 215°) of ethyl di-[2 : 4-dimethylpyrryl]-methane-di-3-carboxylate,

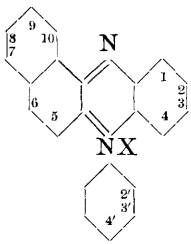


D. F. T.

The *cyclo*Glycylglycines: Direct Synthesis by the Action of Glycerol on the Amino-acids. L. C. MAILLARD (*Ann. Chim.*, 1915, [ix], **3**, 48—120).—The author has applied his method of preparing cyclic anhydrides from amino-acids by heating them with glycerol (compare A., 1912, i, 13; 1914, i, 940; this vol., i, 121) to a number of amino-acids. Sarcosine yielded *cyclo*sarcosylsarcosine [2 : 5-diketo-1 : 4-dimethylpiperazine], m. p. 149—150°. Alanine yielded racemic *cyclo*alanylalanine, [3 : 6-diketo-2 : 5-dimethylpiperazine], m. p. 282—282·5° (corr.). *dl*-Leucine yielded racemic *cyclo*leucyl-leucine [3:6-diketo-2 : 5-di*iso*butylpiperazine], m. p. 271°. In all cases during the heating of the amino-acid with the glycerol, a secondary reaction occurred, substances being generated having an odour very similar to that which is developed during the torrefaction of oil seeds. All the above-mentioned anhydrides have been prepared by other methods and described, and a full account of the literature with reference to them is given in the original. W. G.

Manufacture of ω-Aminomethylquinolines. VEREINIGTE CHININFABRIK, ZIMMER & Co. (D.R.-P. 279193; from *J. Soc. Chem. Ind.*, 1915, **34**, 303).—The nitriles of the quinoline series are reduced by the usual methods. The products have therapeutic value J. C. W.

Quinonimide Dyes. V. Constitution and Colour of the Mono-amines Derived from Phenylnaphthaphenazonium. F. KEHRMANN, R. SPEITEL and E. GRANDMOUGIN (*Ber.*, 1914, **47**, 3205—3215).—Phenylnaphthaphenazonium (annexed formula) gives rise to thirteen mono-amino-derivatives, of which nine are known in the form of salts and one in the form of a salt of the acetyl compound, the best known being rosinduline, the 6-amine. A systematic study has been made of the colours and absorption spectra of these substances. The salts were obtained in varying concentrations of sulphuric acid, and the spectra were tabulated as in the case of the dyes described in the previous papers (see A., 1914, i, 869).



It was soon observed that the isomerides fall into four groups, the individual members of which are constitutionally and optically similar, but differ widely from those of the other groups. The four isomerides in which the amino-groups occupy positions 7, 8, 9, and 10, that is, are attached to the benzenoid part of the naphthalene residue, form the first group. Of these, the 7-, 8- and 9-amines form blue to bluish-green mono-acid salts, lemon-yellow di-acid salts and blood-red tri-acid salts. The 10-amine forms only mono- and di-salts, the azine nitrogen atom in the *peri*-position, owing to steric hindrance, being incapable of salt formation. They all form unstable pseudo-bases under the influence of concentrated alkali hydroxides. A second, incomplete group consists of the 2- and 3-amines, in which the substituents are in the benzene residue of the naphthaphenazine system. These form violet-red mono-acid salts, orange-red to yellowish-green di-acid salts, and violet tri-acid salts. The 3′- and 4′-amines, the external benzene nucleus bearing the substituents, form a third group in which the mono- and di-salts are almost optically identical, being yellow, but differ in solubility, whilst the tri-salts are violet. The optical behaviour of these does not differ to any important extent from that of the un-substituted phenylnaphthaphenazonium, which is in agreement with the rule that salt formation at remote amino-groups scarcely influences the absorption. The 6-amine, rosinduline, the substituent being in the quinonoid part of the naphthalene residue, and the 3-amine, comprise a fourth group, characterised by the intense yellowish-red or blood-red colours of the anhydride forms of the bases, and by the red mono-salts, green di-salts, and red to violet-red tri-salts.

The isomerides, 7, 8, 9, 10, 3′ and 4′ (referring to the position of the amino-group) are undoubtedly *ortho*-quinonoid, which is in agreement with the fact that the di- and tri-salts are practically optically identical with the mono- and di-salts of the unsubstituted parent. Rosinduline and Nietzki and Otto's *iso*rosinduline, the 6- and 3-amines, like *apo*-safranine (*ibid.*), are *para*-quinonoid in the free state and in their mono- and di-salts, but *ortho*-quinonoid in their tri-salts The 2-amine, finally, is certainly *ortho*-quinonoid in its di- and tri-salts, but may be *para*-quinonoid in its mono-salt, which would be unique. J. C. W.

Preparation of Aminobenzothiazolecarboxylic Acids or their Acyl Derivatives. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 277395; from *J. Soc. Chem. Ind.*, 1915, **34**, 269).—Acyl derivatives of the aminobenzothiazoles containing at least one methyl group are oxidised by permanganate in neutral or alkaline solution, and, if desired, the acyl group is subsequently removed. The acylaminobenzothiazolecarboxylic acids so obtained are yellow, and their alkaline salts dissolve in water. They are not diazotisable, but may be used in the preparation of dyes. J. C. W.

Internally Complex Salts. XII. Salt Formation of the Hydroxyguanidines. H. LEY and H. WINKLER (*Ber.*, 1914, **47**, 2945—2947).—It is shown that substituted hydroxyguanidines (acylhydroxylamines) form typical complex metallic salts.

The compounds have been obtained by the condensation of *N*-substituted hydroxylamines with triphenylchloroamidine (Steindorff, A., 1904, i, 452). Thus, phenylhydroxylamine and triphenylchloroamidine were heated in dry toluene, and the hydrochloride which separated was decomposed by ammonia. The product, *hydroxy-*$a\beta\gamma\delta$*-tetraphenylguanidine*, $\overset{\alpha}{\mathrm{N}}\mathrm{Ph}{:}\mathrm{C}(\overset{\beta\gamma}{\mathrm{N}}\mathrm{Ph}_2)\cdot\overset{\delta}{\mathrm{N}}\mathrm{Ph}\cdot\mathrm{OH}$, crystallises in colourless rhombohedra, m. p. 166°, and the *hydrochloride*, in quadratic tablets, m. p. 194°. Ferric chloride gives a deep red coloration with ethereal and a deep blue with alcoholic solutions. The *copper* salt forms chocolate crystals, decomp. 240°; the *nickel* salt forms olive-green, hexagonal plates; the *cobalt* salt is black. The compound is reduced by alcoholic sulphur dioxide to tetraphenylguanidine.

Similarly, *p*-tolylhydroxylamine gives rise to *hydroxy-*$a\beta\gamma$*-triphenyl-*δ *p-tolylguanidine*, $\mathrm{NPh}{:}\mathrm{C}(\mathrm{NPh}_2)\cdot\mathrm{N}(\mathrm{C}_7\mathrm{H}_7)\cdot\mathrm{OH}$, very pale green needles, m. p. 164°, which forms a *copper* salt, reddish-brown, glistening leaflets, and β-benzylhydroxylamine yields *hydroxy-*$a\beta\gamma$*-triphenyl-*δ*-benzylguanidine*, $\mathrm{NPh}{:}\mathrm{C}(\mathrm{NPh}_2)\cdot\mathrm{N}(\mathrm{C}_7\mathrm{H}_7)\cdot\mathrm{OH}$, monoclinic crystals, m. p. 139°; *copper* salt, red; *nickel* salt, greenish-yellow; *cobalt* salt, chocolate.

Phenylcyanamide also condensed with β-benzylhydroxylamine, yielding, apparently, hydroxyphenylbenzylguanidine, which was characterised by a dark brown, crystalline *nickel* salt. J. C. W.

Constitution of Allantoin and Allied Substances. HENRY DRYSDALE DAKIN (T., 1915, **107**, 434—439).—Mendel and Dakin (A., 1910, i, 286) have suggested that the optical inactivity of allantoin is due to tautomerism of the keto-enol type, the formation of the enolic form being accompanied by loss of asymmetry:

$$\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{CO\cdot NH}\end{matrix}\!\!>\!\mathrm{CH\cdot NH\cdot CO\cdot NH_2} \rightleftharpoons \begin{matrix}\mathrm{NH\cdot C(OH)}\\ \mathrm{CO\!-\!\!-\!NH}\end{matrix}\!\!>\!\mathrm{C\cdot NH\cdot CO\cdot NH_2}.$$

Titherley (T., 1913, **103**, 1336) has expressed the opinion that the inactivity is due to tautomerism of a different kind, and the present investigation was therefore undertaken.

Various attempts have been made to resolve 3-methylallantoin and homoallantoin into their active components, but without success. In the course of these experiments the following substances were prepared.

l-α-*Carbamidopropionic acid*, $CH_3\cdot CH(NH\cdot CO\cdot NH_2)\cdot CO_2H$, m. p. 198—200°, obtained by the action of potassium cyanate on *d*-alanine, forms hexagonal prisms and has $[\alpha]_D^{20}$ − 9·6° in aqueous solution; it is readily soluble in hot water, but only about 1—70 in cold water. When this compound is boiled with dilute hydrochloric acid, l-*methylhydantoin*, $CHMe<\begin{matrix}NH\cdot CO\\ |\\ CO-NH\end{matrix}$, m. p. 175—177°, is produced, which has $[\alpha]_D^{20}$ − 50·6° in aqueous solution.

i-α-Carbamidopropionic acid has m. p. 185°, and *i*-α-methylhydantoin, m. p. 150°; when the latter is boiled with dilute barium hydroxide, it is reconverted into α-carbamidopropionic acid. E. G.

Synthesis of Pentazole Compounds. I. I. Lifschitz (*Ber.*, 1915, **48**, 410—420).—When an alcoholic solution of cyanotetrazole (Oliveri-Mandalà, A., 1912, i, 144) and hydrazine hydrate is warmed, ammonia is liberated, and a yellow precipitate of *pentazolylacetohydrazidine*, $\begin{matrix}N:N\\ |\\ N:N\end{matrix}>N\cdot CH_2\cdot C(:NH)\cdot NH\cdot NH_2$, needles, decomp. above 310°, sparingly soluble in all solvents, is produced. On boiling this substance with aqueous potassium hydroxide, more ammonia is evolved and a yellow deposit forms of the *potassium* salt of *pentazolylacetohydrazide*, $\begin{matrix}N:N\\ |\\ N:N\end{matrix}>N\cdot CH_2\cdot C(OH):N\cdot NH_2$, the free hydrazide being a yellow, indistinctly crystalline mass; *barium* salt, brownish-yellow leaflets, which explode when heated. By oxidation of the potassium salt of the hydrazide with potassium permanganate in hot aqueous solution, elimination of the hydrazine group can be effected with formation of a solution of the potassium salt of *pentazolylacetic acid*, $\begin{matrix}N:N\\ |\\ N:N\end{matrix}>N\cdot CH_2\cdot CO_2H$, which was separated as the sparingly soluble *silver* salt.

If a suspension of pentazolylacetohydrazidine in a solution of excess of sodium nitrite is treated with hydrochloric acid, the solution becomes reddish-violet and red crystals of *pentazolyloximinoacetohydrazide*, $\begin{matrix}N:N\\ |\\ N:N\end{matrix}>N\cdot C(:NOH)\cdot CO\cdot NH\cdot NH_2$, separate, which substance readily eliminates a molecule of water, forming the unstable, orange-coloured, crystalline triazolone *compound*, $\begin{matrix}N:N\\ |\\ N:N\end{matrix}>N\cdot C<\begin{matrix}C(OH):N\\ |\\ N---NH\end{matrix}$. Pentazolyloximinoacetohydrazide gives a red acid solution, from which silver nitrate precipitates a deep violet *silver* salt, but barium chloride with hot solutions gives a precipitate of the explosive orange *barium* salt derived from the triazolone compound. By heating pentazolyloximinoacetohydrazide in alcoholic solution with a little hydrochloric acid, hydrolysis is effected with formation of *pentazolyloximinoacetic acid*, $\begin{matrix}N:N\\ |\\ N:N\end{matrix}>N\cdot C(:NOH)\cdot CO_2H$, yellow leaflets insoluble in water. This acid slowly reduces hot ammoniacal silver nitrate solution, being itself oxidised in all probability to pentazolylglyoxylic acid,

$\begin{matrix}N{:}N\\ |\\ N{:}N\end{matrix}\!\!>\!N\cdot CO\cdot CO_2H$; it is decomposed by potassium hydroxide solution with formation of a solution which on acidifying and adding silver nitrate yields an almost colourless precipitate apparently of a double *salt* of silver pentazole and silver hydrogen oxalate,

$$AgN_5,CO_2Ag\cdot CO_2H.$$

The yellow *silver* salt of pentazoiyloximinoacetic acid, obtained by treating a hot aqueous suspension of the acid with silver nitrate solution and nitric acid, was not pure and rapidly changed, giving a red, crystalline, explosive *silver* salt, $N_5\cdot CH{:}N\cdot OAg$; this is soluble in warm potassium hydroxide solution, the resulting colourless solution on subsequent treatment with nitric acid and silver nitrate yielding a colourless, flocculent precipitate apparently of *silver pentazole*, N_5Ag.

D. F. T.

Azoxyphenols. II. A. Angeli (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 30—39).—The paper deals with the constitution of the two azoxyphenols previously described (A., 1914, i, 882). The isolation of the isomeride of lower m. p. (previously given as 107°, now found to be 117°) can be best effected by way of the benzoyl derivative. The *benzoyl* derivative of *α-p*-hydroxyazoxybenzene (m. p. 156°), $C_{19}H_{14}O_3N_2$, forms yellow prisms, m. p. 168°. The *β*-isomeride forms tufts of yellow needles, m. p. 128°. On treating this substance with alcoholic potassium hydroxide, *β-p*-hydroxyazoxybenzene, m. p. 117°, is obtained in the form of yellow prisms.

Both these azoxyphenols react readily with bromine. The *α*-isomeride yields a *monobromo*-derivative, $C_{12}H_9O_2N_2Br$, crystallising in yellow prisms, m. p. 180°, and, by continued action of bromine, a *dibromo*-derivative, $C_{12}H_8O_2N_2Br_2$, which forms yellow, silky needles, m. p. 174°. A *tribromo*-derivative, $C_{12}H_7O_2N_2Br_3$, can only be prepared by brominating 4'-bromo-4-hydroxyazoxybenzene (described in the previous paper); it forms yellow needles, m. p. 197°.

When the dibromo-derivative is reduced with zinc dust and acetic acid, 2 : 6-dibromo-4-aminophenol, aniline and benzanilide are formed, so that the *p*-hydroxyazoxybenzene of m. p. 156° has probably the structure $Ph\cdot NO{:}N\cdot C_6H_4\cdot OH$. The tribromo-derivative mentioned above yields the same dibromoaminophenol together with *p*-bromoaniline, and has therefore the formula $C_6H_4Br\cdot NO{:}N\cdot C_6H_2Br_2\cdot OH$.

The *p*-hydroxyazoxybenzene of m. p. 117° must be assigned the other possible structure, namely, $Ph\cdot N{:}NO\cdot C_6H_4\cdot OH$. By the action of bromine on it a *dibromo*-derivative, $C_{12}H_8O_2N_2Br_2$, m. p. about 141°, is obtained; this differs from the dibromo-derivative already described. At the same time another substance containing bromine, m. p. 173°, is also formed.

R. V. S.

Constitution of the Hydroxyazo-compounds. Action of *as*-Benzoyl-*p*-tolylhydrazine on Benzoquinone and its Homologues. William McPherson and George Weatherworth Stratton (*J. Amer. Chem. Soc.*, 1915, **37**, 906—915).—The quinonehydrazone, formed by the condensation of *α*-benzoylphenylhydrazine with *p*-benzoquinone, and the corresponding hydroxyazo-compound both yield *p*-

hydroxyazobenzene on hydrolysis. It is evident, therefore, that in the hydrolysis of one of the compounds, a migration takes place of the hydrogen atom replacing the benzoyl group. The results obtained by McPherson and Boord (A., 1911, i, 818) show that this migration probably occurs in the hydrazone, and that hydroxyazobenzene has the formula $OH\cdot C_6H_4\cdot N{:}NPh$. This indicates that the molecule,

$$O{:}C_6H_4{:}N\cdot NHPh,$$

is unstable and undergoes rearrangement to the more stable compound $OH\cdot C_6H_4\cdot N{:}NPh$. Attempts have been made to obtain stable compounds of the general formula $O{:}R{:}N\cdot NHR'$, and the action of α-benzoyl-*p*-tolylhydrazine on some *p*-quinones has now been studied. The results show that hydrazones, $O{:}R{:}N\cdot NBz\cdot C_6H_4Me$, are produced which on hydrolysis yield hydroxyazo-compounds, and that the latter furnish benzoyl derivatives isomeric with the original benzoylhydrazones.

α-Benzoyl-β-acetyl-p-*tolylhydrazine*, $C_6H_4Me\cdot NBz\cdot NHAc$, m. p. 135°, obtained by the benzoylation of β-acetyl-*p*-tolylhydrazine, separates in small crystals, and, on hydrolysis, furnishes *α-benzoyl*-p-*tolylhydrazine*, $C_6H_4Me\cdot NBz\cdot NH_2$, m. p. 68—70°, which forms groups of small, white crystals; the *hydrochloride* and *sulphate* of the latter were prepared.

By the action of *p*-tolylhydrazine on benzoquinone, toluquinone, and thymoquinone, the corresponding quinols are produced, whilst in the case of α-naphthaquinone, tolueneazo-α-naphthol is formed.

p-*Benzoquinone-α-benzoyl*-p-*tolylhydrazone*, $O{:}C_6H_4{:}N\cdot NBz\cdot C_6H_4Me$, m. p. 141°, obtained by the condensation of α-benzoyl-*p*-tolylhydrazine with benzoquinone, forms small, yellow crystals and, on hydrolysis, is converted into *p*-tolueneazophenol and benzoic acid. p-*Tolueneazophenyl benzoate*, $OBz\cdot C_6H_4\cdot N{:}N\cdot C_6H_4Me$, m. p. 159°, forms reddish-yellow needles.

2 : 5-*Toluquinone-α-benzoyl*-p-*tolylhydrazone*,

$$O{:}C_6H_3Me{:}N\cdot NBz\cdot C_6H_4Me,$$

m. p. 178°, forms pale yellow crystals, and, on hydrolysis, yields tolueneazo-*o*-cresol, which furnishes a *benzoate*, m. p. 165°.

Thymoquinone-α-benzoyl-p-*tolylhydrazone*,

$$O{:}C_6H_2MePr^{\beta}{:}N\cdot NBz\cdot C_6H_4Me,$$

m. p. 125°, forms pale yellowish-green crystals, and, on hydrolysis, is converted into p-*tolueneazothymol*, m. p. 117°, which forms yellow crystals. p-Tolueneazothymol *benzoate*,

$$OBz\cdot C_6H_2MePr^{\beta}\cdot N{:}N\cdot C_6H_4Me,$$

m. p. 127°, crystallises in short, red needles. E. G.

A New Polyazobenzene. Bruno Valori (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 213—215).—When *p*-aminoazobenzene is oxidised with the calculated quantity of hydrogen peroxide in acetic acid solution, the *polyazo*-derivative, $Ph\cdot N_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot N_2\cdot Ph$, is produced; it crystallises in reddish-gold scales, m. p. 229°. Along with it the compound $Ph\cdot N_2\cdot C_6H_4\cdot N_2O\cdot C_6H_4\cdot N_2\cdot Ph$ (already known) is formed. Both these substances yield on further oxidation with hydrogen peroxide and acetic acid the compound

$$Ph\cdot N_2O\cdot C_6H_4\cdot N_2O\cdot C_6H_4\cdot N_2O\cdot Ph,$$

which is already known. R. V. S.

The Specificity of Caseinogens; a Comparative Study of the Caseinogens of the Cow and Sheep. HAROLD WARD DUDLEY and HERBERT ERNEST WOODMAN (*Biochem. J.*, 1915, 9, 97—102).—By comparing the optical properties of the amino-acids derived from "racemised" cow's and sheep's caseinogen, it is shown that the intramolecular arrangement of the amino-acids in these two proteins is not identical; this probably explains the biological specificity of the caseinogens synthesised by each milk-producing species. The percentage composition of the two proteins examined is practically identical. W. D. H.

Peptone. II. ALESSANDRO BERNARDI and EMMA FABRIS (*Biochem. Zeitsch.*, 1915, **68**, 436—440).—By treatment of a solution of Witte's peptone with cupric hydroxide, two copper salts are obtained, one soluble and the other insoluble in water. From the latter, dissolved in ammonium hydroxide, by means of hydrogen sulphide, a solution can be obtained, from which two different products can be prepared. The one is precipitated by sodium acetate (21%), whereas the other is not so precipitated. S. B. S.

Peptone. III. ALESSANDRO BERNARDI and EMMA FABRIS (*Biochem. Zeitsch.*, 1915, **68**, 441—443).—The peptone (from Witte's peptone) which gives a soluble copper salt was dissolved in water, and the solution was saturated at 0° with hydrogen chloride and then evaporated on the water-bath. From the product so obtained, acetone extracts a substance, from which, by means of cupric hydroxide, a crystalline copper salt of the formula $C_{14}H_{29}O_{20}N_3Cu_2$ has been obtained. S. B. S.

The Mechanism of Biological Oxidation Changes. OSCAR LOEW (*Ber.*, 1914, **47**, 2462—2464).—A reply to Wieland's statement (A., 1914, i, 1007) that, previous to his suggestion as to a possible activation of the hydrogen atoms in biological oxidation processes, it was generally assumed that the changes occurred through activation of the oxygen. D. F. T.

The Chemistry of the Proteolytic Ferments. E. HERZFELD (*Biochem. Zeitsch.*, 1915, **68**, 402—485).—The majority of the investigations were carried out with the employment of Abderhalden's dialysis method and the ninhydrin reaction, the amount of colour yielded by the latter being estimated by the author's spectrophotometric method and the use of a standard glycine solution. It was found that the most active ferment preparations are those which yield the largest amount of substances giving the ninhydrin reaction. The pepsin dialysates give the biuret reaction, whereas the trypsin dialysates do not. The former may therefore be compared with the peptones, and the latter with amino-acids. There was a diminution of the dialysable substances in acid (in the case of pepsin) and alkaline (in the case of trypsin) solutions, which was also marked when the ferments were allowed to act on proteins. These facts lead the author to the conclusion that the dialysable degradation products,

such as peptones and amino-acids, play a part in the hydrolysis of proteins. It was found experimentally (using the dialysis method) that peptones alone can accelerate the proteolytic processes, and there was a certain amount of specificity in their actions; thus, silk peptone could bring about degradation of raw silk, but not of other proteins, and an egg-peptone could cause greater hydrolysis with egg-albumin than with other proteins. A similar catalytic action could also be demonstrated when a synthetic polypeptide was employed (leucylglycine), and a constituent of the peptide could also catalytically bring about the hydrolysis of the peptide; thus both leucine and glycine could bring about hydrolysis of leucylglycine. Furthermore, pure amino-acids and mixtures of the same could play the part of a proteolytic ferment when acting on proteins. The amount of degradation produced was diminished in the presence of 0·5% sodium carbonate. The degradative property was not found in all amino-acids. It was present with glycine, alanine, glutamic acid, leucine, phenylalanine, but absent with aspartic acid and tryptophan. The degradative action could also be traced, when the solid in the dialysate was weighed instead of being estimated by the ninhydrin reaction. The course of hydrolysis was also traced when glycine was allowed to act on a coagulable protein (egg-white). The protein, after varying intervals of incubation, was coagulated, and the non-coagulable substances estimated by the glycine reaction. When sufficient amounts of glycine were employed, the amounts of these progressively increased for a certain time, and then diminished, and the latter fact was taken to indicate that a synthesis takes place when a certain concentration is reached. It is claimed by the author that the protein degradation products in a ferment preparation play an important, although not the sole, part, in the catalysis. It is shown also that heated ferments can also produce a certain amount of degradation. He regards the ferments generally as degradation products. S. B. S.

Organic Derivatives of Silicon. XXIII. Further Experiments on the So-called Siliconic Acids. JOHN ARTHUR MEADS and FREDERIC STANLEY KIPPING (T., 1915, **107**, 459—468).—In an earlier paper (T., 1914, **105**, 681) the authors have given an account of experiments which led them to regard it as probable that all the so-called siliconic acids are complex condensation products of the trihydroxides, $R{\cdot}Si(OH)_3$. A study has now been made of the preparations known as benzyl- and propyl-siliconic acids, and the results support the view that both of these are complex mixtures.

The products of the hydrolysis of benzylsilicon trichloride under different conditions correspond with those obtained similarly from phenylsilicon trichloride, and seem to consist of mixtures of condensation products derived from 3, 4, 5, and 6 mols. of the trihydroxide by the elimination of varying quantities of water.

By the decomposition of propylsilicon trichloride with water at 0°, a mixture was produced, about one-half of which was soluble in ether, whilst the remainder was practically insoluble in all ordinary neutral solvents. The soluble portion became insoluble in a few days, and then seemed to have the composition corresponding with $(Pr{\cdot}SiO)_2O$. It is

considered that both the soluble and insoluble portions are mixtures of condensation products of the trihydroxide, and that the former change to the latter either spontaneously or under the influence of traces of alkali or acid.

The only definite crystalline compounds obtained during this work were the *sodium* salts, $C_7H_7 \cdot SiO_2Na$ and $Pr \cdot SiO_2Na$.

The conclusions are drawn that the trihydric silicols, $R \cdot Si(OH)_3$, undergo condensations analogous to those of the dihydric silicols (Kipping, T., 1912, **101**, 2108, 2125; Robinson and Kipping, T., 1914, **105**, 40, 484), and that the complex mixtures of which the so-called siliconic acids consist contain open- and closed-chain condensation products corresponding with those derived from the silicanediols. The final products of the condensation are insoluble in neutral solvents, have the compositions of the anhydrides, and are probably composed of closed-chain compounds of great molecular complexity. E. G.

The Action of Esters on Magnesium Pyrryl Bromide. V. V. TSCHELINCEV and A. TERENTJEV (*Ber.*, 1914, **47**, 2647—2652; also *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1399—1405).—Magnesium pyrryl haloids, $\begin{matrix} CH{:}C(MgX) \\ | \\ CH{=}{=}{=}CH \end{matrix}\!\!>\!NH$, obtained by the interaction of pyrrole and magnesium methyl iodide (Oddo, A., 1909, i, 672), fail to react with ethyl pyrrole-2-carboxylate, but with the ethyl esters of the homologous fatty acids are found to yield ketones derived from pyrrole by the substitution of an acyl radicle at the 2-position.

The following ketones were prepared in this way: 2-acetylpyrrole, *semicarbazone*, needles, m. p. 190°; 2-propionylpyrrole, *semicarbazone*, tablets, m. p. 181°; 2-butyrylpyrrole, *semicarbazone*, needles, m. p. 131°.

The communication closes with a discussion of the probable mechanism of the reaction. D. F. T.

Preparation of Mercurated Alcohols of the Aromatic Series. ARTHUR ABELMANN (*Ber.*, 1914, **47**, 2931—2935. Compare Dimroth, A., 1902, i, 849).—An application of the Grignard synthesis to the preparation of compounds of aromatic alcohols with mercury. Extraction with chloroform of the insoluble residue of the interaction of Dimroth's acetophenonemercury chloride, magnesium, and ethyl bromide yields a *compound*, $OH \cdot CEtPh \cdot CH_2 \cdot HgCl$, a crystalline, pale yellow powder, sensitive to light, m. p. 129—131° (decomp.). It reacts energetically with the Grignard reagent, and with concentrated sulphuric acid gives a light green coloration, which is destroyed by water. Chloroform extracts from the mother-liquor of its preparation a small proportion of a *compound*, $HgCl \cdot C_6H_4 \cdot C(OH)Et \cdot CH_2 \cdot HgCl$, crystals sensitive to light, m. p. 138—139°. It also reacts energetically with the Grignard reagent, and with concentrated sulphuric acid gives a green coloration, which is destroyed by water.

Similar treatment converts Dimroth's benzophenonemercury chloride into a *compound*, $OH \cdot CPhEt \cdot C_6H_4 \cdot HgCl$, a crystalline powder, m. p. 106° (decomp.). The mercury cannot be precipitated from this substance by ammonium sulphide or hydrogen sulphide. The com-

pound reacts energetically with the Grignard reagent, and with concentrated sulphuric acid it gives a dark green coloration, which is destroyed by water. A. J. W.

Physiological Chemistry.

The Diffusion of Gases through the Lungs of Man. MARIE KROGH (*J. Physiol.*, 1915, **49**, 271—300).—The method for determining the gas diffusion in the human lung during rest and work is described; it is independent of the pulmonary volume up to a certain volume which corresponds with the mean capacity; beyond this, diffusion increases in simple proportion to the volume. It is increased by muscular work independently of any change in the pulmonary mean capacity; this is due to changes in the rate of circulation. The diffusion constant (number of c.c. of oxygen which will diffuse from the alveoli to the blood in one minute at a tension difference of 1 mm.) varies in different individuals from 23 to 43 during rest, and from 37 to 56 during work. Diffusion is sufficient to explain the gaseous interchange in all cases, both at low oxygen pressure and during the heaviest muscular work.

W. D. H.

A Respiration Apparatus for Small Animals. FRANCIS G. BENEDICT (*J. Biol. Chem.*, 1915, **20**, 301—313).—The apparatus is fully described and figured. It gives good results. W. D. H.

The Preservation of Living Red Corpuscles. PEYTON ROUS and J. R. TURNER (*Proc. Soc. expt. Biol. Med. New York*, 1915, **12**, 122—124. Compare this vol., i, 339).—For preserving red blood corpuscles, each species requires a different mixture; sugars, especially sucrose and dextrose, added to the Ringer's solution are preservative, but do not protect the corpuscles from mechanical injury. Dextrin is best for dog's blood, but is useless, or even harmful, for other bloods. If animals are bled and their blood replaced by suspensions of preserved red corpuscles, the vitality of the latter is proved by the fact that they play their normal function in such animals. W. D. H.

Spectroscopic Investigation of the Reduction of Hæmoglobin by Tissue Reductase. DAVID FRASER HARRIS and HENRY JERMAIN MAUDE CREIGHTON (*J. Biol. Chem.*, 1915, **20**, 179—201).—The reduction of oxyhæmoglobin by the reductase contained in liver and other tissues was investigated spectroscopically; the liver juice, especially of birds, proved the most active one examined; reduction of Prussian-blue to the leuco-compound also occurs. Between 10° and 40° the temperature-coefficient is about 2; the process follows the unimolecular law. Tissue-reductase is believed

to be the chief factor in the dissociation of oxygen from oxyhæmoglobin in the body; thus tissue respiration is originated by reductase and completed by oxydases. W. D. H.

Study of the Ninhydrin Reaction in Relation to the Age and Habits of Individuals. JOKICHI TAKAMINE, jun. (*J. Amer. Chem. Soc.*, 1915, **37**, 946—949).—Abderhalden has shown that the blood contains a "Schutzferment," which is only brought into activity by some special and extraneous agency. The author has now found that another ferment is also present in the blood, which is shown by the triketohydrindene hydrate (ninhydrin) reaction to vary in amount according to the age and habits of the individual. Experiments on the blood serum of sixty-eight persons have shown that the ferment increases greatly with age, and is present in considerable quantities in the blood of heavy drinkers and of those suffering from syphilis. The increase of the ferment with age was also observed in the case of rats, rabbits, and horses. E. G.

The Non-protein Nitrogenous Compounds of the Blood in Nephritis with Special Reference to Creatinine and Uric Acid. VICTOR C. MYERS and MORRIS S. FINE (*J. Biol. Chem.*, 1915, **20**, 391—402).—In nephritis, retention of non-protein nitrogenous compounds and their accumulation in the blood often occurs, especially in uræmic conditions. The present paper deals with uric acid and creatinine; in the cases dealt with, high concentrations of these two substances were met with, although uræmia may not be present or imminent. Whether methylguanidine (from the creatinine) may be a possible cause of uræmia is discussed, but not yet established. The rise in the uric acid is often greater than in gout, but gouty symptoms were absent. An increase in creatine noted suggests an increase of tissue-destruction. In the cerebrospinal fluid, the urea and creatinine approach the concentrations found in other fluids in uræmia, but creatine and uric acid are low or absent. W. D. H.

The Inhibition Produced by Certain Sera on the Coagulating Power of Rennet. AAGE CHRISTIAN THAYSEN (*Biochem. J.*, 1915, **9**, 110—131).—The inhibition of rennet by normal horse serum is not produced by two inhibitory substances (true anti-substance and pseudo-antirennet), as Korschun considers, neither is it an adsorption phenomenon, as Hedin thinks. The hydrogen-ion concentration of the serum is highly important for its inhibiting power. Normal rabbit's serum behaves in the same way as normal horse serum. The inhibiting power of a rennet antiserum, made by immunising rabbits with rennet, cannot be due to the presence of a true anti-substance, as this serum also tends to show the characteristics of normal horse serum. W. D. H.

Tryptic Digestion by Activated Serum. J. BRONNENFENNER and K. M. SCOTT (*Proc. Soc. expt. Biol. Med. New York*, 1915, **12**, 137—138).—Normal serum shows no digestive power, but tryptic

activity may be demonstrated by the removal of antitrypsin. This may be shown with boiled placenta, or fresh placenta cells. The antitrypsin may be removed by adsorption with starch or kaolin, or by extraction with chloroform. W. D. H.

The Auxo-lipase of Serum. KWANJI TSUJI (*Biochem. J.*, 1915, **9**, 53—65).—The addition of serum to pancreatic extract or to inactive lipase accelerates markedly lipoclastic action. The name auxo-lipase is given to the constituent of serum responsible for this action; it is not identical with the co-enzyme contained in pancreatic extracts, since it is non-dialysable, and destroyed by incineration. It is thermostable. Mellanby and Woolley have suggested that serum activates merely because it contains antitrypsin, and thus prevents the destructive action which trypsin exerts on lipase, but no relationship could be demonstrated between the antitrypsin and the auxo-lipase of serum. W. D. H.

The Action of Serum on the Lipase of Pancreatic Juice. J. A. SHAW-MACKENZIE (*J. Physiol.*, 1915, **49**, 216—221).—The action of serum in accelerating lipoclastic activity is a pronounced one, and can be demonstrated, not only with pancreatic extracts, but with the juice itself. This is not due, as Mellanby and Woolley consider, to the antitrypsin of the serum protecting the lipase from destruction by trypsin, because antitryptic power and the power of accelerating lipoclastic activity do not always run parallel; moreover, serum which has been heated to a temperature which destroys antitrypsin is still able to accelerate lipoclastic activity, both of the juice and of extracts. The lipoclastic activity of the fresh juice is always low, and evidence is adduced that the enzyme in the fresh juice is mainly in an inactive condition (pro-lipase); after the juice has been heated to destroy its lipoclastic action, the thermostable co-enzyme is still present, and the addition of such juice to fresh juice accelerates the fat-splitting power of the latter. W. D. H.

Tissue Juice as a Hæmostatic. ALFRED F. HESS (*Proc. Soc. expt. Biol. Med. New York*, 1915, **12**, 117).—Tissue juice prepared by extracting tissues (especially brain) with salt solution hastens clotting *in vivo* after injection, or *in vitro*. Applied locally, it is a potent hæmostatic, and is specially useful in hæmophilia. W. D. H.

Digestion of the Proteins of Cooked Meat in the Dog. II. EDGARD ZUNZ (*Biochem. J.*, 1915, **9**, 17—35).—The products of digestion in the dog's stomach after feeding on cooked beef were separated by a method of centrifugalisation. The results, in comparison with those obtained by the older methods, showed a larger proportion of proteoses and a smaller proportion of acid-metaprotein, peptones, and abiuretic products. In the duodenum, the results are not affected by the method used; metaprotein is absent, or present only in traces; about one-fifth of the non-coagulable

nitrogen is in the state of proteose, and the remainder as peptone and abiuretic products. The figures given differ somewhat according to the kind of meat given, and details are also presented showing the partition of nitrogen in different regions of the stomach.

W. D. H.

The Digestion and Absorption of Protein and Fat in Normal and Depancreatised Animals. ERNEST WILLIAM HENDERSON CRUICKSHANK (*Biochem. J.*, 1915, **9**, 138—155).—Depancreatisation reduces digestion and absorption of nitrogen (22%) and fat (67%). The addition of pancreas to the diet is beneficial. The accompanying diabetes is reduced if the pancreas is removed in two stages.

W. D. H.

Inactive Lipase and the Nature of its Co-enzyme. NOBUYOSHI UMEDA (*Biochem. J.*, 1915, **9**, 38—52).—Rosenheim showed that lipase as contained in glycerol extracts of the pancreas can be separated by filtration into an inactive thermolabile moiety on the filter, and a thermostable co-enzyme in the filtrate. The major part of the co-enzyme consists of inorganic salts, and the phosphates in the ash represent the most active constituents of the co-enzyme; organic substances, probably organic phosphates, are also concerned in the activation. W. D. H.

The Ferments of the Pancreas. V. The Carbohydrate Ferments of the Pancreatic Juice. JOHN MELLANBY and V. J. WOOLLEY (*J. Physiol.*, 1915, **49**, 246—265).—Pancreatic juice free from carbon dioxide breaks down starch into dextrin (25%) and maltose (75%). This is facilitated by the presence of calcium and sodium chlorides. The juice has no action on maltose. But if hydrochloric acid is added, dextrose is also formed as the hydrogen ion concentration rises; as much as 54% of dextrose may be formed under optimal conditions; the amount of dextrin also falls. The opinion is advanced that only one enzyme (amylopsin) is present, but when acid is added, the acid and the enzyme are associated, and the further action is due to the action of the association. This is believed to occur during normal digestion. The juice has no action on sucrose or lactose. W. D. H.

The Metabolism of Vegetarians as Compared with that of Non-Vegetarians of like Weight and Height. FRANCIS G. BENEDICT and PAUL ROTH (*J. Biol. Chem.*, 1915, **20**, 231—241).—In men vegetarians, the average heat production per diem per kilo. of body-weight was 25·5, or per square metre of surface 798 calories; in non-vegetarians, the respective figures were 26·4 and 828; in women, the small difference just noted in men disappears. The respiratory quotient was practically the same throughout.

W. D. H.

The Metabolism of Athletes as Compared with Normal Individuals of Similar Weight and Height. F. G. BENEDICT and H. MONMOUTH SMITH (*J. Biol. Chem.*, 1915, **20**, 243—252).—Athletes have a somewhat higher metabolism than non-athletes both per

kilo. of body-weight (26 : 24·4) and per square metre of surface (863 : 807). The katabolism is proportional, not to the surface of the body, but to the active mass of protoplasmic tissue.

W. D. H.

A Comparison of the Basal Metabolism of Normal Men and Women. F. G. Benedict and L. E. Emmes (*J. Biol. Chem.*, 1915, **20**, 253—262).—The metabolism of men is about 5 or 6% greater than that of women of similar age, weight, and height. Men have a larger proportion of active protoplasmic tissue. W. D. H.

Factors Affecting Basal Metabolism. Francis G. Benedict (*J. Biol. Chem.*, 1915, **20**, 263—299).—Body weight plays an important part, but the heat production is not directly proportional to it. The variations between body surface and metabolism are far outside possible errors in formulæ; tall individuals usually have a greater metabolism than short ones of the same weight. All the facts point to the amount of active protoplasmic tissue being the main factor. In youth, there is greater cellular activity, and so a higher metabolism; sleep reduces it. There is also a diurnal variation related to activity. Other factors considered are fasting, diet, and work, but all tend to the same general conclusion.

W. D. H.

The Metabolic Relationship of the Proteins to Dextrose. N. W. Janney (*J. Biol. Chem.*, 1915, **20**, 321—350).—Each protein produces a definite amount of dextrose in the phloridzinised animal. The various yields represent 50 to 80% by weight of the protein administered. These yields approximate to the ratios which the glucogenetic amino-acids of the proteins in each case bear to the total amino-acids as estimated after hydrolysis. Vegetable and animal proteins under optimal conditions are metabolised at the same rate. All the extra dextrose and nitrogen are eliminated by the ninth hour after ingestion. W. D. H.

Carbohydrate Metabolism. VIII. The Influence of Hydrazine on the Utilisation of Dextrose. Frank P. Underhill and Albert G. Hogan (*J. Biol. Chem.*, 1915, **20**, 203—210).—Hydrazine sometimes causes hypoglycæmia in rabbits, as in dogs. Inanition causes no change in the amount of blood-sugar. When dextrose is given two days after the administration of hydrazine, its utilisation is markedly retarded, whether the amount of blood-sugar was previously low or not. But this does not explain the hypoglycæmia. W. D. H.

Carbohydrate Metabolism. IX. The Influence of Hydrazine on the Glyoxalase Activity of the Liver. Frank P. Underhill and Albert G. Hogan (*J. Biol. Chem.*, 1915, **20**, 211—215).—The glyoxalase activity of the liver is not markedly altered by the action of hydrazine. The disappearance of glycogen from the liver, and of sugar from the blood, is therefore still unexplained.

W. D. H.

Metabolism in Experimental Diabetes. VICTOR HENRY KINGSLEY MOORHOUSE, SIDNEY WENTWORTH PATTERSON, and MARJORY STEPHENSON (*Biochem. J.*, 1915, **9**, 171—214).—The increase in total metabolism varies with the severity of the diabetes produced, but averages 15 to 20%. The rise in the respiratory quotient which normally follows ingestion of sugar is less, or is absent, after removal of the pancreas; this indicates that complete oxidation of sugar does not occur. The increase in the excretion of acetone substances runs parallel to the rise in the increase of total metabolism and of the D : N ratio. W. D. H.

Metabolism of Amino-acids in the Organism. I and II. Action of Muscular Tissue on Amino-acids Added to Circulating Blood and to Circulating Ringer's Solution. UGO LOMBROSO (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 57—62, 148—153).—Circulation in the muscles of the dog of blood containing up to 1% of glycine or alanine is accompanied by diminution in the amount of the amino-acid. The greater proportion of the amino-acid thus lost is deposited unchanged in the muscular tissue, whilst the remainder is partly burnt, with formation of ammonia, and partly utilised to form substances which cannot be titrated in presence of formaldehyde. When the amino-acid is circulated in solution in Ringer's liquid, a similar diminution, which may amount to as much as 12%, occurs in the proportion of amino-acid in the circulating liquid. The amount of the latter also decreases, and the total loss of amino-acid may exceed 50%, the whole of this, with the exception of 1—2%, being found deposited in the tissue; here, also, the liquid always contains small proportions of ammonia after the circulation. T. H. P.

The Influence of the Plane of Protein Intake on Growth. E. V. MCCOLLUM and MARGUERITE DAVIS (*J. Biol. Chem.*, 1915, **20**, 415—428).—The curves shown indicate that the lowest plane of protein intake on a milk diet in young rats which leads to no loss of weight is 3% of the food mixture; between 3 and 8% there is a progressive increase in the rate of growth; if the protein supplied by wheat is 6% of the food mixture, growth occurs at half the normal rate; 2·5% of protein from desiccated eggs does not prevent loss of body-weight. The protein from wheat embryo (4%) compares favourably with the same protein intake from milk powder, and is rather better than 6% from the entire wheat kernel. W. D. H.

The Comparative Nutritive Value of Certain Problems in Growth, and the Problem of the Protein Minimum. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (*J. Biol. Chem.*, 1915, **20**, 351—378).—The experiments, like the previous ones carried out by the authors, were conducted on rats, and follow much the same lines. The sole nitrogenous food was a single protein, and the inefficiency of some of these to promote growth is strikingly illustrated by tables and charts; in many cases the inefficient protein is rendered efficient, or less inefficient, by the addition to the diet

of amino-acids lacking or scanty in the diet; thus, the inefficiency of zein is counteracted by tryptophan, of caseinogen by cystine, of edestin by lysine. Much importance appears to be attached to the lysine content. The general question of the protein minimum has been usually investigated on mixed diets; the problem where a single protein is given in the food is complicated by the composition of the protein; this is well illustrated by comparing lactalbumin and caseinogen; much more of the latter is wanted than the former, in which the proportions of the amino-acids are admirably correct. W. D. H.

The Influence of Natural Fats on Growth. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (*J. Biol. Chem.*, 1915, **20**, 379—389).—These experiments on growing rats taking a "synthetic diet" bring out the following points. The failure of lard to promote growth (as butter-fat, egg-yolk fat, and cod-liver oil do) cannot be attributed to deteriorating changes arising from heat or chemical agents in manufacture. If butter-fat is heated with steam, its growth-promoting efficiency is not altered. Beef-fat is better than lard.

If butter-fat and beef-fat are subjected to fractional crystallisation from alcohol, the growth-promoting component remains in the mother liquor, or "oil" fractions. Fractions containing the fats with high melting points are ineffective. W. D. H.

Reciprocal Action of Sodium, Potassium, and Calcium Ions on the Frog's Heart. TAKUZO SAKAI (*Zeitsch. Biol.*, 1914, **64**, 505—548. Compare A., 1914, i, 768).—Increasing the potassium content of an isotonic solution perfusing the isolated ventricle of a frog's heart results in a decreased rate of beating, lowering of the height of contraction, and inhibition of the "extra systoles." Increasing the proportion of calcium in the perfusion fluid produces exactly the reverse effects. Sodium chloride exerts a similar action to that of potassium chloride, except for lower concentrations. Reducing the concentration of sodium salt below the normal also reduces the height of contraction and the frequency of ventricular beat, and eventually brings the ventricle to rest. The reciprocal action of calcium and of sodium and potassium salts does not depend wholly on the ratio of their concentrations, but also on the absolute quantities of the substances present in the perfusion fluid.

The sinus differs markedly from the ventricle in its response to changes in the composition of the perfusion fluid. Increasing the calcium content usually slightly lowers the rate of beat, whilst other similar variations in the sodium and potassium content of the perfusion fluid do not appear to have any distinct effect.

H. W. B.

Fatty Acid Metabolism in the Liver. IV. The Relation of the Iodine Values of Mesenteric and Kidney Fatty Acids to those of Liver Fatty Acids in Pregnant and Lactating Rabbits. R. COOPE and V. H. MOTTRAM (*J. Physiol.*, 1915, **49**, 157—161).—The fatty acids of mesenteric fat normally show wide variations

in their iodine values. Those from kidney show marked constancy; those of the liver give intermediate values, as would be expected; at or about the time of parturition, the values lie near to those of the mesenteric fatty acids; the conclusion previously reached, that infiltration of the liver with depôt fatty acids occurs, is confirmed. W. D. H.

Lignoceric Acid from Carnaubon. Otto Rosenheim and Hugh Maclean (*Biochem. J.*, 1915, **9**, 103—108).—The name carnaubon was given by Dunham to a protagon-like substance obtained from kidneys; later, he separated from it carnaubic acid, $C_{24}H_{48}O_2$, as well as stearic and palmitic acids; he regarded carnaubon as a triaminomonophosphatide.

In the present research, it was established that the carnaubic acid is identical with lignoceric acid; stearic and palmitic acids were not found, but phrenosinic acid, $C_{25}H_{50}O_3$, was discovered. The elementary composition of carnaubon is very variable; it is really, like protagon from brain, a mixture of galactosides (which furnish the two acids just mentioned) with sphingomyelin; in brain-protagon the galactosides, and in kidney-protagon (carnaubon), the sphingomyelin, preponderate. There is no reason why the names carnaubon and protagon need be retained for these mixtures of lipoids. W. D. H.

Action of Suprarenals on Renal Secretion. D. Cow (*Proc. Roy. Soc. Med.* [*Therap. Pharm. Sect.*], 1915, **8**, 1—3).—In cats after removal of one suprarenal, excitation of the sciatic nerve caused the intact suprarenal capsule reflexly to pour its secretion into the circulation; the majority of the viscera had been removed, and means taken so that the secretion should find its way, not into the general circulation, but only to the kidneys. An abrupt diminution of the urinary flow occurred out of all proportion to the lessened amount of blood passing through the kidney vessels; there was shrinkage of the kidney, and marked contraction of the capsule of Bowman and of the uriniferous tubules. W. D. H.

The Specific Affinity of Thyroid Cells for Iodine. David Marine (*Proc. Soc. expt. Biol. Med. New York*, 1915, **12**, 132—134).—The affinity of thyroid tissue for iodine is well known. In the present experiments, dogs' surviving spleens, kidneys, and thyroids were perfused at 37° wih a mixture of blood and Ringer's solution, to which potassium iodide was added. The iodine, before and after perfusion, was estimated in the tissue; in spleen and kidney there was no increase; but the thyroid retained a large amount, especially in cases where there was marked hyperplasm of the thyroid tissue. This does not occur when the thyroid tissue is dead; death and autolysis occur in the thyroid a few hours after removal from the body; whether the iodine is combined as thyreoglobulin has not yet been ascertained. W. D. H.

Chemical and Physico-chemical Properties of Muscle and of Muscular Juices. VI. Phosphorus Content of White and Red Striated Muscle. G. QUAGLIARIELLO (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 348—352).—Both the white and red striated muscle of birds and of the rabbit contain phosphorus in amount corresponding with about 2% of phosphoric oxide, calculated on the dry matter; this proportion is appreciably higher than with other animals. The content of total phosphorus is slightly greater in the white than in the red muscle, but in the case of birds, phosphatides represent about 11% of the total phosphorus of white muscle and about 22% of that of red muscle. With the rabbit, the corresponding proportions are 13% and 17% (compare Katz, A., 1896, ii, 377). T. H. P.

The Fate of Fatty Acids in the Survival Processes of Muscle. GEORGE WINFIELD (*J. Physiol.*, 1915, **49**, 171—179).—There is no evidence that any change occurs in the fat of amphibian muscle during survival which would account for the development of lactic acid which occurs. This is true for uninjured muscle during simple rigor under aërobic conditions, and during prolonged stimulation under anaërobic conditions, even although excitability is then restored by means of oxygen.
W. D. H.

The Cholesterol Content of the Tissues of Growing Rats when under Various Diets. PERCY EDWARD LANDER (*Biochem. J.* 1915, **9**, 78—96).—Rats just beginning to feed themselves contain 0·15% cholesterol; three weeks later, after a diet of bread and oatmeal, this rises to 0·2. On a pure synthetic diet without cholesterol, no growth occurs, but the cholesterol percentage in the body remains unchanged. If half the caseinogen in the diet is replaced by cholesterol-free protein obtained from testes, and lecithin is added, no growth or change in the cholesterol content takes place. When milk was added to the diet, the rats increased 66% in weight in twenty-three days; the cholesterol of the milk is eagerly picked out by the body and stored; there was no evidence that it was formed synthetically; if only half the milk is given plus cholesterol, growth was not so rapid, and about one-tenth of the cholesterol given was stored. On the addition of cholesterol and cholesteryl esters to the synthetic diet, together with lecithin and Lemco, growth did not proceed, or the weight decrease, in spite of a storage of about one-tenth of the cholesterol eaten.
W. D. H.

Composition of Human Urine During a Two Weeks' Fast. RINJI WATANABE and RENPEI SASSA (*Zeitsch. Biol.*, 1914, **64**, 373—408).—The authors have compared the composition of the urine passed daily by a Japanese rhapsodist whilst undergoing a hunger cure with that passed during the preceding and the succeeding seven days. Only water was allowed during the fasting period. The body-weight decreased from 50·3 to 44·1 kilo., and in the

succeeding seven days increased again to 47·4 kilo. The total nitrogen increased during the first few days of the fast, and then declined to a constant minimum in the second week. The preliminary rise in total nitrogen excretion is probably accounted for by the fact that the subject of the experiment was of muscular build, with apparently only a little fat in the body, and consequently the commencement of the fast was equivalent to a change from his usual vegetable diet to one involving the consumption of his own proteins.

During the fast, the ammonia and creatinine nitrogen were increased both absolutely and relatively to the total nitrogen; the amino-acid nitrogen was correspondingly diminished. Uric acid nitrogen decreased at the beginning of the fast, and then steadily rose until, at the end, its ratio to the total nitrogen was normal. The amount of excreted purine bases was practically constant throughout the fast, whilst the chlorides and phosphates were considerably diminished. A marked acidosis occurred at the onset of the starvation period, with appearance of acetone and acetoacetic acid; when food was again taken, the acetone and acidosis promptly disappeared. Exactly the reverse occurred in the case of indican, the reaction for which became negative soon after the commencement of the fast, and only became positive when food was again taken. H. W. B.

Saline Diuresis. S. Yagi and M. Kuroda (*J. Physiol.*, 1915, **49**, 162—170).—Saline diuretics were injected intravenously, and diuresis on one side was limited by compression of the renal artery; this was accompanied with a fall in chloride excretion. The urea was less affected, and the excretion of sulphates still less. When the general blood-pressure is reduced by vagus stimulation, the same results are seen, and these are comparable to those observed when the ureter on one side is partly obstructed. They are regarded as compatible with the view that the glomerular filtrate is subjected to selective absorption as it passes along the ureter (*sic*, ? renal tubules). W. D. H.

The Excretion of Antigen. Agnes Ellen Porter (*Biochem. J.*, 1915, **9**, 1—8).—Egg-white introduced parenterally into a rabbit is excreted in the urine unchanged in chemical properties, but varying in specificity; it may retain its full properties as an antigen, or these may be only partly retained, or altogether lost. This variation points to a physical rather than a chemical explanation of the precipitin reaction. W. D. H.

The Respiratory Quotient in Diabetes. Graham Lusk (*Proc. Soc. expt. Biol. Med. New York*, 1915, **12**, 125—126).—When dextrose arises from protein in diabetes, the oxidation is different from the normal. When the D : N ratio in the urine is 3·65, the respiratory quotient for protein falls from 0·801 to 0·634. The six sugar-forming amino-acids (glycine, alanine, aspartic acid, glutamic acid, proline, and arginine) comprise about 64·5% of meat protein

(Osborne), and this would yield 44·4 grams of dextrose from 100 grams of meat. This would indicate a D : N of 2·75, and explain the origin of 76% of the maximal sugar production from protein. The respiratory quotient of 64·5 grams of sugar-forming amino-acids, when oxidised normally, would be 0·915, but when they yield dextrose it sinks to 0·675; that of the non-sugar-forming amino-acids would be 0·716. The amounts in meat of cystine and serine, both of which yield sugar, are unknown. W. D. H.

Guanidine or Methylguanidine as a Toxic Agent in the Tetany following Parathyroidectomy. D. Noël Paton, Leonard Findlay, and David Burns (*Proc. physiol. Soc.*, 1915, xvii—xviii; *J. Physiol.* **49**).—Deficiency of calcium salts does not appear to be the sole factor in the causation of tetany after removal of the parathyroids; there is evidence of the presence of a toxin, which is counteracted by calcium. On the hypothesis that the toxic agent may originate from the creatine of muscle, various guanidine compounds were injected into cats, rats, and rabbits. All of those employed (guanidine hydrochloride and carbonate, and methylguanidine nitrate) produced typical tetany, and the effects were removed by the administration of calcium salts. W. D. H.

Antagonism of Drugs. A. R. Cushny (*Proc. Roy. Soc. Med.* [*Therap. Pharm. Sect.*], 1915, **8**, 6—8).—The quantitative relation of the antagonism of atropine and pilocarpine on salivary secretion in dogs was found to be in the proportion 0·5 : 5. The antagonism is regarded as an example of mass action, and not of the chemical law of multiples. The view that toxins and antitoxins form an actual chemical combination is held to require reconsideration. W. D. H.

Action of the Oil and Seeds of Croton Elliotianus. J. Theodore Cash and Walter J. Dilling (*J. Pharm. expt. Ther.*, 1914, **6**, 235—281).—This variety of croton comes from British East Africa. The seed contains a fixed oil and several proteins. The action of the seed is purgative and slightly diuretic. The oil is less active than the seeds, but more uniform in action. Doses of 0·04—0·06 c.c. act as a mild laxative, whilst 0·1 c.c. causes vigorous purgation. There is also a slight hæmolytic action. Its relatively non-irritant action makes it a valuable drug. W. D. H.

Phenylacetylglutamine, a Metabolic Product of the Human Body after Administration of Phenylacetic Acid. H. Thierfelder and C. P. Sherwin (*Ber.*, 1914, **47**, 2630—2634).—Although phenylacetic acid has been observed to be eliminated by dogs and hens respectively as phenylaceturic acid and phenylaceto-ornithuric acid (see Totani, A., 1910, ii, 880), its behaviour in the human system has not been examined. After administration of phenylacetic acid, it is found that the human urine contains phenylacetylglutamine and phenylacetylglutamine-carbamide, the latter substance being easily resolvable into its constituents, phenylacetylglutamine and carbamide. D. F. T.

Action of Diuretics of the Methylxanthine Group on Healthy Persons on Various Diets. Robert Widmer (*Zeitsch. Biol*, 1914, **64**, 315—372).—The author has studied particularly the diuretic action of the sodium salt of theophyllineacetic acid on a man maintained for successive periods on a meat and on a milk diet. A great difference was observed in the relative amounts of sodium chloride and water eliminated in the normal urine on these two diets. It is accounted for by the diuretic action of the purines in the meat diet, and a peculiar sparing mechanism which reduces the urinary output of chlorides and of water on the milk diet. The action of the diuretic at each period appears to be physiological, and results in an increased elimination of the urine normally passed on the particular diet employed. The water is, however, eliminated more quickly than the sodium chloride.

H. W. B.

The Action of Veratrum. Russell J. Collins and Paul J. Hanzlik (*Proc. Soc. expt. Biol. Med. New York*, 1915, **12**, 134—135).—The chemical effects of *Veratrum album* resemble the pharmacological, slowing and weakening the heart's action. These take place independently of "toxic" symptoms (nausea and vomiting).

W. D. H.

The Toxicity of Sodium Pyrophosphate Administered with the Food, with a Note on Toxic Cotton-seed Meal. William Legge Symes and John Addyman Gardner (*Biochem. J.*, 1915, **9**, 9—16).—Sodium pyrophosphate given with the food to rabbits, cats, and rats is devoid of the toxic action which follows intravenous injection. This confirms Gamgee and others. In a sheep, however, it proved lethal. The toxic action when the salt is given by the mouth is wholly due to its alkalinity, and not to the acid radicle. Rats died from intestinal inflammation when fed on toxic cotton-seed meal; the phosphate content of the meal was low; the poisonous principle has not yet been discovered.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Behaviour of Bacteria towards Purified Animal and Vegetable Proteins. JOEL A. SPERRY and LEO F. RETTGER (*J. Biol. Chem.*, 1915, **20**, 445—459).—Bainbridge states that certain aërobic and facultative aërobic bacteria are unable to decompose pure animal proteins. This is confirmed, and it is further shown that the same is true for very active putrefactive bacteria, and for pure vegetable proteins, such as edestin. Solutions of such proteins may undergo complete proteolysis if they contain peptone

or some other nitrogenous food necessary for bacterial development; the responsible enzyme originates from the bacteria during their multiplication. Pure proteins are not antiseptic, but the explanation advanced is the stability of their molecules.

W. D. H.

Bacteriological Investigations of Soils. A. Wojtkiewicz (*Centr. Bakt. Par.*, 1914, ii, **42**, 254—261).—The examination of several soils showed that the number of organisms is lowest in winter and highest in spring, the average increase being 30—40%. Assimilation of nitrogen varied considerably, the minimum fixation being in winter and the maximum in the autumn. Daily variations of temperature have no influence on nitrogen-fixation.

No very definite results were obtained with regard to nitrification, putrefactive power, and decomposition of carbamide. The denitrifying power of the soils was found to be greatest in the autumn and lowest in the spring. Production of carbon dioxide does not seem to be influenced by variations in the numbers of organisms present in the soil.

N. H. J. M.

Antagonism between Anions as Affecting Soil Bacteria. Charles B. Lipman and Paul S. Burgess (*Centr. Bakt. Par.*, 1914, ii, **42**, 502—509).—In a sandy soil, very slight, if any, antagonism was found to occur for the nitrogen-fixing flora when sodium carbonate and sodium chloride are mixed. The same results are obtained with sodium chloride and sulphate, when the chloride is the constant toxic factor, but not when the sulphate is used as the constant factor. Between sodium carbonate and sulphate there is no antagonism, however the salts are combined.

The concentrations at which nitrogen fixation ceases are lower when the salts are mixed than when employed singly. The nitrogen-fixing flora differ totally from the ammonifying and nitrifying flora of the same soil as regards antagonism between anions, and the resistance of the nitrogen-fixing organisms to salts is far greater than that of the other organisms referred to.

N. H. J. M.

The Lime-Magnesia Ratio. I. Effects of Calcium and Magnesium Carbonates on Ammonification. W. P. Kelley (*Centr. Bakt. Par.*, 1914, ii, **42**, 519—526).—Experiments on the ammonification of dried blood and soy-bean cake mixed with various soils (laterites), to which different amounts of calcium and magnesium carbonates (separately and mixed) were added. It was found that, although most of the soils contained an excess of magnesium over calcium, addition of calcium carbonate produced only slight stimulation, whilst in many cases magnesium carbonate produced considerable stimulation. In these soils, therefore, the lime-magnesia ratio seems to have little or no importance in relation to ammonification. In accordance with the observations of Lipman that the effect of magnesium carbonate sometimes depends on the nature of the nitrogenous material, it was found

that the stimulation induced by magnesium carbonate was more marked with dried blood than in the case of soy-bean cake.

Experiments with a soil composed largely of coral sand showed that relatively small amounts of magnesium carbonate depressed the yield of ammonia for dried blood.

In four other soils it was found that magnesium carbonate had a depressing effect in two, and a stimulating effect in the other two. Dolomite and limestone had very little effect, if any.

In Hawaiian soils, the magnesium present is largely in the form of hydrous silicates. N. H. J. M.

The Lime-Magnesia Ratio. II. Effects of Calcium and Magnesium Carbonates on Nitrification. W. P. KELLEY (*Centr. Bakt. Par.*, 1914, ii, **42**, 577—582).—The results of nitrification experiments varied with the different soils employed. In some there was considerable stimulation with calcium carbonate, in others none at all. Magnesium carbonate was toxic in five of the soils, and had very little effect in the others. In the soils and with the nitrogenous materials with which calcium carbonate was most stimulating, magnesium carbonate was most toxic.

Dolomite was not in any of the soils toxic, and in one of the soils produced marked stimulation, whilst magnesium carbonate, in the same soil, was extremely toxic.

In all of the soils employed, except perhaps the coral soil (preceding abstract), the soluble organic salts of magnesium, produced from the magnesium carbonate and organic acids in the soil, would probably become fixed to a considerable extent, with liberation of potassium, sodium and calcium, so that the concentration of the different constituents in the soil solution would be greatly changed by adding magnesium carbonate, and this would affect bacterial action. In the coral soil, it is probable that addition of magnesium carbonate would result in an excess of magnesium in the soil solution over the other bases; hence the toxicity to ammonification.

The slight effect of calcium carbonate in the soils containing only very small amounts of carbonate is attributed to the large amounts of iron and aluminium hydroxides present (Ashby, *J. Agric. Sci.*, 1906, **2**, 52). N. H. J. M.

Influence of Arsenic on the Nitrogen-fixing Powers of the Soil. J. E. GREAVES and H. P. ANDERSON (*Centr. Bakt. Par.*, 1914, ii, **42**, 244—254. Compare A., 1914, i, 237).—The nitrogen-fixing powers of soils is stimulated by arsenic in the form of lead and sodium arsenates, arsenic trisulphide and zinc arsenite, the greatest stimulation being produced by lead arsenate and the least by zinc arsenite. Paris-green has no stimulating action in any of the concentrations employed, and is very toxic when the amount reaches 120 per million. Lead arsenate is not toxic in concentrations of 400 per million.

Soils containing large amounts of organic matter fix as much nitrogen in presence of arsenic, and without mannitol, as in presence of mannitol without arsenic.

Only one type of *Azotobacter* was isolated which was stimulated by arsenic, the stimulation being due to the organism utilising more economically its source of carbon in presence than in absence of arsenic. In soils, the stimulating effect of arsenic may be due, in part, to the destruction of injurious species. N. H. J. M.

Influence of Organic Acid on Yeast. Iv. Buromski (*Centr. Bakt. Par.*, 1914, ii, 530—557).—Yeast which is developed on a mineral substratum with peptone and organic acids does not form zymase, but increases the amount of oxidising ferments, especially when succinic acid is employed. When the cultures are transferred to solutions containing sugar, they continue to develop, and in one to three days fermentation begins, which is at first very feeble. The commencement of fermentation varies with the acids employed, being usually earlier and more vigorous on quinic acid, whilst on tartaric acid it is weakest.

Yeasts from acids which no longer ferment sugar only recover the power of producing zymase after some generations on sugar. The reversion to their former state does not take place simultaneously with all yeast cells, but only in the case of those in which the newly-acquired properties are less established.

N. H. J. M.

Preparation of Peptone by Decomposition of the Cells of Beer Yeast and the Rôle of this Peptone in Fermentation. Eug. Vlahuță (*Bull. Acad. Sci. Roumanie*, 1914–15, **3**, 123—131).—A résumé of the various theories advanced to explain the processes of fermentation, from the time of Liebig up to the present time, is given. The author is of the opinion that a peptone obtainable from yeast cells is capable of bringing about fermentation. This peptone is obtained by adding in small quantities 100 grams of fresh yeast, which has been submitted to 50—100 atmos. pressure, to 70% sulphuric acid. The acid was kept cold by a freezing mixture, and after all the yeast had been added, the emulsion was allowed to remain in the freezing mixture for three hours, and finally it was allowed to come to atmospheric temperature, where it remained for three days. The emulsion was then added drop by drop to 1500 c.c. of ice-cooled water. Barium hydroxide was then added until a faintly alkaline solution was obtained. The barium sulphate was removed by filtration, and the excess of barium hydroxide carefully precipitated by the addition of the exact amount of dilute sulphuric acid. In this way, a yellowish, faintly acid solution of peptone is obtained, which gives the biuret and all other reactions of protein substances. The fermentative action is tested by taking 20 c.c. of the solution, adding 0·2 c.c. of toluene and quantities of dextrose or sucrose, and measuring the volume of carbon dioxide liberated in a measured time. Definite fermentation occurred, and from a table of comparison with results obtained with Buchner's preparations, it is obvious that the action is about one-fortieth that of these preparations. J. F. S.

Formation of Acetaldehyde by Atmospheric Oxygen in the Alcoholic Fermentation of Sugar. EDUARD BUCHNER, KURT LANGHELD, and SIEGFRIED SKRAUP (*Ber.*, 1914, **47**, 2550—2555).—The small quantities of acetaldehyde which can be detected as formed in the fermentation of sugar by yeast extract in the presence of sodium phosphate depend for their formation on the access of air, and the occurrence of this substance is prevented by the application of an atmosphere of hydrogen or nitrogen. Acetaldehyde is therefore only of secondary formation in alcoholic fermentation, and is not an essential intermediate product (compare Kostytschev, A., 1912, ii, 589, 860; see also A., 1914, i, 635, 1034). D. F. T.

The Composition of the Arsenious Gases Producible by Penicillium Moulds. PETER KLASON (*Ber.*, 1914, **47**, 2634—2642).—The paper opens with a summary of the investigations on this subject since the first mention by Gmelin in 1839 of the possibility of poisoning by wallpapers coloured with arsenic compounds, such as Schweinfurt-green.

The view has been expressed by various workers (for example, Biginelli, A., 1901, i, 20) that the volatile compound containing arsenic is diethylarsine, but a repetition of the earlier work, in which the gas was absorbed, as previously, by mercuric chloride solution, and also by nitric acid, indicates that the gaseous product is diethylcacodyl oxide, $(AsEt_2)_2O$; absorption by mercuric chloride gives an additive compound, or causes oxidation to ethylcacodylic acid if the solution of mercuric chloride is dilute, whilst nitric acid effects oxidation to ethylcacodylic acid. The identity between the latter substance as prepared by synthesis, and by the action of a *Penicillium* culture on arsenious acid, seems to be satisfactorily proved. The diethylcacodyl oxide is unaccompanied by any trace of arsine, for the latter substance, even in minute quantity, gives a pale yellow coloration to a 1% mercuric chloride solution, whereas the gases formed by the culture give with a solution of this concentration a colourless liquid and a crystalline deposit of mercurous chloride. D. F. T.

Methods for Killing Vinegar Animalculæ. J. F. SACHER (*Chem. Zeit.*, 1914, **38**, 1021—1022).—The undesirable animalculæ which are often found in vinegar can readily be killed by heating for a few minutes to 45°. At 40—42° they commence to show signs of death, but if this temperature is not maintained for some length of time they appear to be capable of recovery. Exposure for two hours to direct sunlight was also found sufficient to destroy completely all the living forms present, but this method is only applicable to finished vinegar, as *Mycoderma aceti* are also injuriously affected by light of short wave-length. Complete exclusion of air caused the death of all animalculæ in from six to eight weeks, but, apart from this, carbon dioxide was found to be without effect on them. One per cent. of sodium chloride acted fatally within twenty-four hours, but lesser concentrations either

required longer time or were uncertain in action. Potassium chloride has no toxic action. Similar toxic effects were observed with 2·5% of sodium sulphate, 1% of sodium nitrate, and 0·68% of sodium hydroxide, whilst the corresponding potassium compounds were innocuous. Small quantities of strongly dissociated acids also rapidly killed the organisms. Calcium and magnesium peroxides, which have been recommended for this purpose, must be used in concentrations of from 1—2%. A very stable peroxidised compound of acetic acid and the peroxide is produced, and is the active agent in destroying the vinegar animalculæ. A sharp limit of the alcoholic strength which the organisms can tolerate was not found. Many are killed in a few hours by the addition of 8% of alcohol, but others, particularly the females, remain alive for days. A concentration of 14% of alcohol is, however, fatal to all within eighteen hours. G. F. M.

Copper Spraying Fluids. H. Fonzes-Diacon (*Compt. rend.*, 1915, **160**, 528—530).—A discussion of the anticryptogamic powers of different copper spraying fluids, such as Bordeaux and Burgundy mixtures, prepared under varying conditions. The acid spraying fluids are rich in the basic, bluish-green, tetracupric sulphate, and their anticryptogamic power is very high. The alkali spraying fluids only contain a little of this basic sulphate, and, on exposure to air, only give very little copper sulphate, and consequently have only a low anticryptogamic power. W. G.

Action of the Hydrogen Ion and of Some Anions on the Germinative Period of Avena sativa. F. Plate (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 166—171).—The experiments were made with solutions of various concentrations of phosphoric, sulphuric, nitric, and hydrochloric acids. The effects of the anions diminish in the order given. The hydrogen ion is chiefly active in the root, and localises itself there, whilst the anions are found chiefly in the growing point. R. V. S.

Action of Individual Chlorides on the Germinative Period of Avena sativa. F. Plate (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 234—238. Compare A., 1914, i, 367, 639, 912).—The paper describes experiments on germinating plants of *A. sativa* in solutions of diverse concentrations of the chlorides of the alkali metals. The results are set forth in tables, and discussed and compared with those obtained in the author's experiments with nitrates. R. V. S.

Action of Ammonium Compounds on the Germination of Avena sativa. F. Plate (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 146—148).—Correction of certain numerical data of the author's previous paper (A., 1914, i, 912). T. H. P.

The Membrane as a Seat of Chemical Action. A. Tschirch (*Arch Phrm.*, 1914, **252**, 537—546).—The author's theory that the

formation of secretions occurs, without the aid of the plasma, in the schizogenous secretory receptacles of the resinogenous layer, has been denied by Euler on the ground that synthetic processes cannot take place without the assistance of the protoplasm. The author refutes this opinion by means of well-established facts dealing with the chemical performances of membranes; moreover, the latter contain a whole series of the most diverse membranins, such as lichen-membranin, pectin-membranin, etc., which are frequently transformed one into another, although they are not in direct contact with the plasma.

The author now expresses the definite opinion that membranins are polysaccharides containing calcium, magnesium, and potassium atoms in complex combination.

The following observation strengthens the author's conviction that chemical action occurs in membranes. When a germinating plant is loosened from the soil, and the root is rapidly washed in water, the root-hairs retain particles of the soil very tenaciously, this being effected by a mucilage membrane which has been formed on the outer wall of the root-hair, and in which the particles are firmly embedded. The utilisation of the inorganic constituents of the soil, therefore, occurs in a membrane which is separated from the plasma by a cellulose wall; this membrane possesses the power of selecting individual constituents of the soil.

Certain plant membranes, therefore, especially those belonging to the original layer of the walls, or derived therefrom, undoubtedly have the power of synthesis; an essential condition, however, is that the membrane must have a colloidal character. C. S.

The Antioxydase of Tomatoes. LUBIMENKO (*Compt. rend.*, 1915, **160**, 479—481).—The author has determined the peroxydase content of the juice of tomatoes at different stages in their development by measuring the intensity of the blue coloration produced with guaiacum in alcoholic solution in the presence of hydrogen peroxide. The peroxydase content increases steadily up to the time when the fruit begins to change from green to red, when it disappears. If, however, the juice from a red tomato is left in contact with toluene for one day, it shows the presence of a considerable amount of peroxydase. The toluene can be replaced by formalin, ether, or chloroform. The author considers that the tomato contains an antioxydase, which increases in amount as the fruit ripens, paralysing the action of the peroxydase, but which is more sensitive to the influence of different antiseptics than is the peroxydase. These antagonistic enzymes are unequally distributed in the different tissues of the fruit, as is shown by applying the guaiacum test to the freshly-cut surface of a section through the middle of a red tomato. W. G.

Organic Chemistry.

Nature and Classification of the [Solid] Paraffins of Petroleum and Methods for their Extraction. M. A. Rakuzin (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1544—1566).—For the investigation of the solid paraffins present in petroleum, the author has subjected the petroleum to centrifugation and to filtration through a Chamberland candle and through various powdered, porous materials. The various products separated have been examined microscopically.

All the higher, so-called solid paraffins, resin and carbonaceous matter are removable from petroleum by centrifugation (compare A., 1909, ii, 153). When boiled in a reflux apparatus with the finely powdered porcelain of a Chamberland candle, petroleum loses all its solid paraffins, but the resin is retained. Experiments were also made with floridin (aluminium magnesium hydrosilicate).

The results indicate the presence in petroleum of soft, medium and hard paraffins of crystalline structure and do not confirm Zalozeski's theory (*Zeitsch. angew. Chem.*, 1888, 126), according to which crude petroleum contains only amorphous "protoparaffins," which consist of isomerides of normal paraffins, and are converted into crystalline "pyroparaffins" of the normal series on distillation. T. H. P.

Oxidation of the Methyl Group in Unsaturated Compounds with an Open Carbon-atom Chain. B. K. Mereshkovski (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1244—1250).—The formation of oxalic acid when a mixture of *iso*butylene and methylene*cyclo*propane is oxidised by means of 0·5% potassium permanganate solution (*ibid.*, 1913, **45**, 2072) was regarded by the author as the result of the following series of changes taking place with the methylene*cyclo*propane: $CH_2{:}C\langle^{CH_2}_{CH_2}$ $\longrightarrow$ $OH{\cdot}CH_2{\cdot}C(OH)\langle^{CH_2}_{CH_2}$ $\longrightarrow$ $CO_2H{\cdot}CO{\cdot}CH_2{\cdot}CO_2H \longrightarrow 2CO_2H{\cdot}CO_2H$.

It has, however, been pointed out to the author that oxalic acid might be formed quite simply from the *iso*butylene, and that, in general, this acid may be obtained by the oxidation of all organic compounds, its appearance being, therefore, valueless as an indication of structure.

The author has investigated the influence, under conditions otherwise similar, of the concentration of the oxidising agent on the velocity of oxidation of the methyl group in unsaturated compounds. Experiments made with propylene, *iso*butylene, and trimethylethylene show that, when permanganate solutions of different concentrations are employed, totally different oxidation products are obtained. The general behaviour is the same with the three hydrocarbons. At 0° and with 0·5% permanganate solution, the methyl group is not oxidised and no trace of oxalic acid is formed. As the concentration

is increased, oxidation of the methyl group takes place to an increasing extent and at 3% proceeds rapidly. With 7% permanganate solution, the oxalic acid constitutes about 48% of the total acids formed; with higher concentrations, the velocity of oxidation of the methyl group in compounds containing an unsaturated linking becomes equal to the velocity of oxidation of the unsaturated linking itself.

The common practice of employing oxidising agents in high concentrations with the object of accelerating the action is, therefore, inadmissible, as also is the use of high temperatures, even when the concentration of the oxidising agent is low.

The above results indicate the direction in which an explanation is to be sought for many observations on the oxidation of unsaturated hydrocarbons made by various investigators and as yet incapable of interpretation. T. H. P.

Convenient Apparatus for Chlorination with Phosphorus Pentachloride. STUART P. MILLER and FRANKLIN C. GURLEY (*J. Amer. Chem. Soc.*, 1915, **37**, 1361).—In the course of some work on sulphonic acid derivatives, the following method was devised for carrying out chlorination with phosphorus pentachloride. The material is placed in a thick-walled filter-flask, the side-arm of which is attached to a filter-pump. Suction is applied, the phosphorus pentachloride is added, and the substances are ground together with a piece of glass rod. By this means the escape of hydrogen chloride into the air is avoided. If only small quantities of material are available, a thick-walled test-tube with a side-tube may be used. E. G.

Vinylethyl Alcohol [Δ^{γ}-Butenyl Alcohol]. THEODORA ZELINKA (*Monatsh.*, 1914, **35**, 1507—1509).—Δ^{γ}-Butenyl alcohol,

$$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH,$$

may be obtained in 15—20% yield by gradually adding allyl bromide to magnesium turnings and paraformaldehyde covered with ether, and heating the resulting product for several days on the water-bath (compare Wagner, A., 1894, i, 563). It has b. p. 113—114°, and reacts with phosphorus tribromide, yielding *Δ^{γ}-butenyl bromide*, b. p. 98·4—98·6°/750 mm. F. B.

Action of Sulphuric Acid on Higher Diprimary Glycols. ADOLF FRANKE and FRITZ LIEBEN (*Monatsh*, 1914, **35**, 1431—1443).—It has been shown previously by Lieben (A., 1902, i, 336) that the action of sulphuric acid on $\alpha\beta$-glycols yields aldehydes or ketones, whilst $\alpha\delta$- or $\alpha\varepsilon$-glycols are converted into the corresponding cyclic oxides. $\alpha\gamma$-Glycols, on the other hand, show an irregular behaviour and yield, according to their constitution, either ketones, aldehydes, or oxides, together with cyclic dioxides derived by the loss of water from two molecules of the glycol. The authors have now extended the investigation to $\alpha\zeta$- and $\alpha\theta$-glycols, and find that both yield cyclic oxides, which, however, contain either five- or six-membered rings.

aζ-Hexylene glycol, prepared by reducing ethyl adipate with sodium and alcohol, has b. p. 150°/12 mm., m. p. 42°, and is converted by the action of 50% sulphuric acid into aδ- or *aε-hexylene oxide*,

$$O<\begin{matrix}CHEt\cdot CH_2\\ CH_2-CH_2\end{matrix}\text{ or }O<\begin{matrix}CHMe\cdot CH_2\\ CH_2-CH_2\end{matrix}>CH_2,$$

a mobile liquid, having b. p. 104·5—106°/749 mm., $D_4^{21\cdot1}$ 0·8537. It has not yet been found possible to decide definitely between these two formulæ, but the behaviour of the compound on oxidation with potassium permanganate is in better agreement with the first formula. The main products of the oxidation consist of acetic and succinic acids; small amounts of propionic, formic and oxalic acids are also formed, together with an oily *acid*, probably $C_6H_{12}O_3$, or the corresponding lactone. An oxide having the structure represented in the second formula should yield glutaric acid on oxidation; no trace of this acid, however, could be found amongst the products of oxidation.

aθ-Octylene glycol, prepared by reducing methyl suberate, has b. p. 164°/12 mm., m. p. 60°, and is converted by 50% sulphuric acid into aδ- or *aε-octylene oxide*,

$$O<\begin{matrix}CH(CH_2Pr^{\alpha})\cdot CH_2\\ CH_2-\!\!-\!\!-\!\!-CH_2\end{matrix}\text{ or }O<\begin{matrix}CHPr^{\alpha}\cdot CH_2\\ CH_2-CH_2\end{matrix}>CH_2,$$

a mobile liquid which has b. p. 155—157°/752 mm., $D_4^{22\cdot7}$ 0·8516, and on oxidation with potassium permanganate yields mainly succinic and propionic acids, together with small quantities of formic, butyric, oxalic, and probably valeric acids. F. B.

Synthesis of Heptane-aη-diol and of Some Derivatives of Hexane, Heptane and Octane. R. Dionneau (*Ann. Chim.*, 1915, [ix], **3**, 194—268).—For the most part a more detailed account of work already recorded (compare A., 1906, i, 134; 1907, i, 747; 1910, i, 353; 1913, i, 719). In the last part of the paper the author has summarised the physical properties of the diprimary glycols,

$$HO\cdot[CH_2]_n\cdot OH,$$

and their derivatives from ethanediol to nonanediol, bringing out the following points. The boiling points of the glycols, their diacetates, and their corresponding dibromo- and di-iodo-compounds and dimethyl ethers, lie on smooth curves for each group, showing a steady increase with rise in molecular weight. The glycols are divided into two groups with respect to their melting points, those with an even number of carbon atoms having higher melting points than those with an odd number of carbon atoms next higher in the series. The densities of the diacetates, dibromides, and di-iodides also lie on smooth curves, descending as the molecular weights increase. The indices of refraction of the dibromides and di-iodides show a steady decrease with increase in molecular weight; those of the dimethyl ethers, on the other hand, steadily increase with rise in molecular weight. The density curve of the dimethyl ethers is somewhat irregular, and there is but slight variation from one member to another. In the case of the diacetates, dibromides, di-iodides and the dimethyl ethers, the curves showing the variation in molecular volumes and molecular refractions are in each case straight lines. W. G.

Synthesis of α-Glycerophosphoric Acid. O. Bailly (*Compt. rend.*, 1915, **160**, 663—666).—The author has repeated Cavalier's work (compare A., 1895, i, 638) on the behaviour of allylphosphoric acid towards bromine and his attempts to prepare glycerophosphoric acid from the resulting dibromoglycerophosphoric acid, and has confirmed his results. He has succeeded in preparing pure calcium α-glycerophosphate by the following method. To an aqueous solution of sodium allylphosphate (18 grams) at 15°, 500 c.c. of 3% aqueous potassium permanganate were added, and after several hours the precipitated manganese dioxide was filtered off. The filtrate was made neutral to phenolphthalein, and a concentrated aqueous solution of calcium chloride (12 grams) was added. Any precipitated calcium phosphate was filtered off, and the calcium α-glycerophosphate precipitated by addition of alcohol, being purified by solution and reprecipitation. The barium and strontium α-glycerophosphates were also prepared and their solubilities determined as below.

	Grams of salt in 100 grams of saturated solution.	
Salt of	α-Salts.	β-Salts.
Calcium	4·95 at 15°	1·72 at 15°
Barium	1·83 at 17°	57·6 at 12°
Strontium	1·79 at 16°	2·35 at 15°

The value given for the solubility of calcium α-glycerophosphate is considerably higher than that given by King and Pyman (T., 1914, **105**, 1238). W. G.

Molecular Weights of the Monochloroacetic Acids and αβ-Dibromopropionic Acids, Compounds with Double Melting Points. B. Tollens (*Ber.*, 1915, **48**, 489—496).—The molecular weights of the stable and labile forms of these acids have been determined by cryoscopic and ebullioscopic methods in water, ether and acetone, that is, at temperatures below the transition points, and in benzene and ethylene dibromide. In agreement with other workers, it is found that the acids are monomolecular in the first three solvents, but somewhat associated in the last two. The differences between the acids are therefore not connected with the size of the molecules. J. C. W.

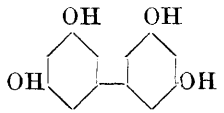
The Systems: Barium Oxide–Acetic Acid–Water and Magnesium Oxide–Acetic Acid–Water. Junichi Iwaki (*Mem. Coll. Sci. Kyoto*, 1914, **1**, 81—88).—The equilibrium relationships have been examined at 25° by analysis of the saturated solutions and of the solid residues. The results obtained point to the existence of the following acid salts which have not hitherto been described:

$3Ba(CH_3\cdot CO_2)_2,3CH_3\cdot CO_2H,11H_2O$;
$Ba(CH_3\cdot CO_2)_2,2CH_3\cdot CO_2H$; $2Mg(CH_3\cdot CO_2)_2,3CH_3\cdot CO_2H,3H_2O$; $5Mg(CH_3\cdot CO_2)_2,10CH_3\cdot CO_2H,7H_2O$. The acid salts described by Villiers (this Journ., 1877, 428) as having the composition $Ba(CH_3\cdot CO_2)_2,CH_3\cdot CO_2H,4H_2O$ and $Ba(CH_3\cdot CO_2)_2,2CH_3\cdot CO_2H,2H_2O$ are probably identical with the two barium salts indicated by the author's observations. H. M. D.

Transformation of Butyric Acid into Propyl Butyrate by the Action of Light. E. Paternò (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 674—675; *Gazzetta*, 1915, **45**, i, 389—390).—The benzopinacone formed from benzophenone and butyric acid under the influence of sunlight (compare Paternò and Chieffi, A., 1911, i, 65) is accompanied by propyl butyrate. The conversion of benzophenone into benzopinacone is apparently effected by means of hydrogen withdrawn from the carboxyl groups of two molecules of butyric acid, the resulting compound, Pr·CO·O·O·CO·Pr, then losing the elements of carbon dioxide to form propyl butyrate. Such a reaction is new in photochemistry, but it occurs during the electrolysis of fatty acids, and is similar to the action of iodine on silver butyrate, which also yields propyl butyrate. It may serve to explain the formation of esters in plants. T. H. P.

The Abietic Acid of Spanish Colophonium. J. Sureda Blanes (*Anal. Fis. Quim.*, 1915, **13**, 176—179).—Spanish colophony contains abietic acid, $C_{19}H_{28}O_2$, white crystals, m. p. 153—154°, $[\alpha]_D^{16} - 57{\cdot}8°$. It is identical with the acid present in American colophony, and can be isolated by the method of Easterfield and Bagley (T., 1904, **85**, 1247). It contains two double linkings, being converted by the hydrogenation method of Willstätter and Hatt into hydroabietic acid, $C_{19}H_{32}O_2$, m. p. 176—179°, $[\alpha]_D^{16}$ −16·85°, identical with the acid obtained by Maly in 1866 by reduction with sodium amalgam and alcohol. A. J. W.

New Method for the Preparation of Tartronic Acid. O. von Friedrichs (*Ber.*, 1914, **47**, 2983—2986).—With the hope of obtaining oxidation products which would give a clue to the constitution of diresorcinol (Barth and Schreder, A., 1879, 633) the technical substance has been treated with fuming nitric acid. The main product is found to be tartronic acid, which would support the annexed symmetrical formula.



The best yield (48%) of tartronic acid is obtained by adding 1 gram of diresorcinol in small portions to 10 c.c. of cold, fuming nitric acid, allowing the mass to become warm, and, after the vigorous action is over (five to ten minutes), evaporating the excess of nitric acid. The crude tartronic acid is freed from a trace of a nitro-compound by means of ether, in which the latter is only sparingly soluble.

The author has since shown that the product was really anhydrous oxalic acid (*Ber.*, 1914, **47**, 3369; A., 1915, i, 233). J. C. W.

Cuprous Salts of Oxygen Acids and a New Method for Preparing Cuprous Salts. Lloyd C. Daniels (*J. Amer. Chem. Soc.*, 1915, **37**, 1167—1171).—Very few cuprous salts of oxygen acids are known, and it is sometimes erroneously stated that such compounds do not exist. The best known of these salts is the red cuprous

sulphite, Cu_2SO_3,H_2O, and it is now shown that this compound can be employed for the preparation of other cuprous salts.

When cuprous sulphite is sprinkled little by little into a hot solution of oxalic acid, carbon dioxide is evolved, and the colour of the solid changes from red to brown. *Cuprous oxalate*, $Cu_2C_2O_4,2H_2O$, which is thus obtained, becomes grey when first heated, then turns greenish-grey and loses traces of water, and finally undergoes violent decomposition. The grey substance has the same composition as the original brown compound.

Cuprous oxalate can also be prepared by digesting cuprous oxide with solution of oxalic acid. E. G.

Action of Magnesium *tert.*-Amyl Chloride on Ethyl Oxalate. (Mlle.) E. Venus (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1332—1336). —Like magnesium *tert.*-butyl chloride (compare Egorova, A., 1910, i, 90), magnesium *tert.*-amyl chloride exhibits reducing properties, its reaction with ethyl oxalate taking place according to the equations: $CO_2Et\cdot CO_2Et + C_5H_{11}\cdot MgCl = C_5H_{11}\cdot C(OEt)(OMgCl)\cdot CO_2Et$, the latter then giving either $C_5H_{11}\cdot CH(OMgCl)\cdot CO_2Et \longrightarrow$

$$C_5H_{11}\cdot CH(OH)\cdot CO_2Et \longrightarrow C_5H_{11}\cdot CH(OH)\cdot CO_2H$$

or $C_5H_{11}\cdot CH(OEt)\cdot CO_2Et \longrightarrow C_5H_{11}\cdot CH(OEt)\cdot CO_2H$. The reduction of the OEt or the OMgCl group is effected by means of magnesium hydrogen chloride, which, as is shown by the liberation of amylene, is formed according to the equation: $C_5H_{11}\cdot MgCl = MgHCl + C_5H_{10}$.

Ethyl α-hydroxy-ββ-dimethylvalerate, $CMe_2Et\cdot CH(OH)\cdot CO_2Et$, is a liquid, b. p. 78—79°/8 mm., D_0^0 0·9668, D_{21}^{21} 0·9501, D_0^{21} 0·9462, and has the normal molecular weight in freezing benzene. The corresponding *acid*, $C_7H_{11}O_3$, forms shining, transparent leaflets, m. p. 72—73°, and exhibits normal cryoscopic behaviour in acetic acid; its *calcium* salt was analysed.

α-Ethoxy-ββ-dimethylvaleric acid, $CMe_2Et\cdot CH(OEt)\cdot CO_2H$, forms transparent plates, m. p. 107—108°, and has the normal molecular weight in freezing water. T. H. P.

Electrolysis of Dicarboxylic Organic Acids: Acetylenedicarboxylic Acid. B. L. Vanzetti (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 611—615. Compare A., 1904, i, 850; 1906, i, 624; 1907, i, 823; 1908, i, 939).—Electrolysis of acetylenedicarboxylic acid or its potassium salt yields acetylene, carbon monoxide and dioxide and oxygen, the acetylene being formed at the anode. After the first few hours, the amount of carbon dioxide evolved remains almost constant. Carbon monoxide is liberated at first in large amount, but this diminishes later, then increases, and finally decreases rapidly to zero; the quantity of oxygen varies inversely with the carbon monoxide, the total volume of the two gases remaining approximately constant. A small proportion of fumaric acid is also formed.

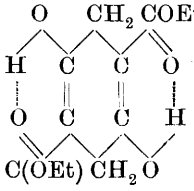
The electrolytic decomposition of the acid or its potassium salt seems to be complete, the two CO_2 groups of the carboxyl radicles being separated and the central carbon of the molecule undergoing oxidation to carbon monoxide. T. H. P.

The Constitution of Ethyl Succinylsuccinate and its Halogen Derivatives. A. HANTZSCH (*Ber.*, 1915, **48**, 772—785).—To ethyl succinylsuccinate have been variously attributed the structures $CO_2Et\cdot CH<^{CO\cdot CH_2}_{CH_2\cdot CO}>CH\cdot CO_2Et$ and

$$CO_2Et\cdot C<^{C(OH)\cdot CH_2}_{CH_2\cdot C(OH)}>C\cdot CO_2Et.$$

By a combination of the spectroscopic method of investigation with an examination of the halogen compounds formed by the substance, the author is led definitely to decide in favour of the latter constitution.

In the presence of alcohol the ester combines readily with bromine, yielding a tetrabromide, and although in certain other solvents the unsaturated character of the substance appears to be more or less lacking, the compound is probably dienolic throughout, for optical examination of the various solutions shows them to be almost identical, whilst at the same time the absorption of ethyl dimethylsuccinylsuccinate, $CO_2Et\cdot CMe<^{CO\cdot CH_2}_{CH_2\cdot CO}>CMe\cdot CO_2Et$, is quite different. The extraordinary stability of the dienol structure of ethyl succinylsuccinate is referred to the possibility of ring formation through partial valencies as indicated by the annexed formula.



Although the tetrabromide of ethyl succinylsuccinate is easily formed in alcoholic solution, the compound cannot be isolated, and the corresponding tetrachloride which is produced from the alcoholic solution of the tetrabromide by treatment with silver chloride also cannot be separated. The solutions of both tetrahaloids give a reddish-brown coloration with ferric chloride. Although no indication of the formation of a dihalogen derivative involving the saturation of only one of the two ethylenic linkings could be obtained, a second class of halogen compound was producible; the most definite example of this new type is *ethyl succinylsuccinate β-dichloride*, which is formed by the action of chlorine on an ethereal suspension of the ester at $-15°$. The *β-dichloride* is remarkable in behaving as a relatively stable saturated substance, giving no reaction with ferric chloride, and unlike the above-mentioned tetrachloride of the α-series, from which it differs entirely in absorption spectrum, it can be obtained in a solid state, needles, decomp. at 106°. On account of its characteristic chemical behaviour and distinct absorption spectrum, the β-dichloride is believed to have the structure $CO_2Et\cdot CCl<^{CH_2\cdot C(OH)}_{C(OH)\cdot CH_2}>CCl\cdot CO_2Et$ with a para-linking. It was not found possible to isolate the corresponding β-dibromide, but experiments in this direction yielded two dibromides of yet another type, the action of bromine vapour on an aqueous alcoholic suspension of ethyl succinylsuccinate giving two *dibromides* of ethyl dihydroxyterephthalate, $C_6H_2Br_2(OH)_2(CO_2Et)_2$, the less stable α-isomeride undergoing fission into its components, bromine and ethyl dihydroxyterephthalate, more readily than the β-isomeride, into which it can

also undergo spontaneous transformation. The formation of these isomerides is attributed to the primary formation of the tetrabromide with subsequent loss of 2 mols. of hydrogen bromide, and the α- and β-isomerides are respectively represented

$$CO_2Et\cdot C\begin{matrix}<\\>\end{matrix}\begin{matrix}CH\cdot CBr(OH)\\C(OH)=CH\end{matrix}\begin{matrix}>\\<\end{matrix}CBr\cdot CO_2Et$$

and $CO_2Et\cdot CBr\begin{matrix}<\\>\end{matrix}\begin{matrix}CH:C(OH)\\C(OH):CH\end{matrix}\begin{matrix}>\\<\end{matrix}CBr\cdot CO_2Et$; the enolic nature of these isomerides is demonstrated by their capacity to add bromine, but the expected hexabromide is so unstable that only its decomposition product, namely, ethyl dibromobenzoquinonedicarboxylate, $C_6O_2Br_2(CO_2Et)_2$, was separable from the product. D. F. T.

Polarimetric Researches on the Modifications that Tartaric Acid Undergoes during Fusion. G. Bruhat (*Ann. Chim.*, 1915, [ix], **3**, 121—140).—The author has followed the changes which take place in tartaric acid on fusion by frequent measurements of the rotation of an aqueous solution of the superfused acid over a long period of time. The chemical changes which take place are the same whether boric acid is present or not in this solution, the influence of the latter tending only to modify the rotatory power of the solutions. This change in the solution of the superfused acid takes place in two stages: (1) a rapid modification finished in a few hours, marked in both cases by a diminution in the rotation, slightly less rapid in the presence of boric acid; (2) a slow modification, lasting several months, which produces a diminution of the rotation for pure tartaric acid, and an increase in the presence of boric acid, there being an increase in the dispersion in the latter case. The author considers that the second phase is due to the transformation of ditartaric acid into tartaric acid, and this is borne out by measurements at frequent intervals of the acidity of the solution, which increases slowly with the time for several months. The first phase is apparently unaccompanied by any change in acidity, and is probably due to the conversion of metatartaric acid into tartaric acid. W. G.

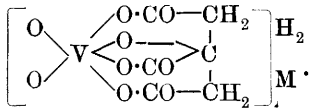
Magnesium Citrate and the So-called Basic Magnesium Citrates. E. Léger (*Compt. rend.*, 1915, **160**, 660—663).—Methods for preparing three hydrates of magnesium citrate are given. On saturating a hot, concentrated solution of citric acid with magnesium carbonate, the *hydrate*, $Mg_3(C_6H_5O_7)_2,13H_2O$, slowly crystallises out. The rate of crystallisation cannot be accelerated by sowing the solution with a crystal of the required hydrate and the formation of the tridecahydrate is probably due to the slow hydration of a heptahydrate, which is very soluble in cold water. If a concentrated solution of the magnesium citrate is heated for twenty-four hours on a water-bath a nonahydrate, $Mg_3(C_6H_5O_7)_2,9H_2O$, slowly separates as a crystalline precipitate (compare Kämmerer, this Journ., 1874, 252). This hydrate is also obtained in voluminous prisms by heating the solution of magnesium citrate at 110°. On mixing boiling alcoholic solutions of magnesium acetate (3 mols.) and citric acid (2 mols.), the *heptahydrate*, $Mg_3(C_6H_5O_7)_2,7H_2O$, is obtained, which is soluble in two parts of cold water, its aqueous solution depositing crystals of the tridecahydrate after a time. The heptahydrate is also

obtained by leaving the anhydrous salt in a moist atmosphere for one month. The tridecahydrate loses $11H_2O$ at 110°, and the last $2H_2O$ only at 150—155°. The nonahydrate loses nothing at 110° and is only dehydrated at 175°. It is insoluble in water, but soluble in ammonia, from which solution, in a vacuum over sulphuric acid, *magnesium ammonium citrate*, $Mg_3(C_6H_5O_7)_2,2NH_3,5H_2O$, is deposited in the form of plates, soluble in water. Its solution when exposed to air loses ammonia and gives the tridecahydrate. The author has repeated Kärnmerer's work on the basic magnesium citrates (*loc. cit.*), but finds no evidence in favour of the existence of these substances. W. G.

Complexes of Vanadic Acid with Citric Acid. G. A. Barbieri (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 724—729).—Solutions containing ammonium, sodium or potassium metavanadate and citric acid deposit crystalline substances of the composition

$$M_2O,V_2O_5,2C_6H_6O_6,2H_2O,$$

which readily lose their water below 100°. The ammonium compound is moderately soluble in water, but only sparingly so in presence of ammonium chloride or sulphate, and similar behaviour is shown by the sodium and potassium compounds. Addition of silver nitrate to one of these solutions yields a precipitate containing silver and vanadic and citric acids. These compounds are consequently complex in character. Prandtl and Hess (A., 1913, i, 815) show that vanadic acid dissolves in many alcohols, such dissolution being accompanied by esterification, and that particularly stable compounds are given by the tertiary alcohols. It is, therefore, regarded as probable that the union of the vanadic and citric acids takes place at the expense of the hydroxyl group of the citric acid, and that the three secondary valencies of the central vanadium atom are satisfied by the three carboxyl groups of the citric acid,



These salts are, therefore, acid salts. Treatment under suitable conditions of an alkali citrovanadate with silver nitrate yields the normal silver salt, $[V(O_2)(C_6H_4O_6)]Ag_3$.

Ammonium citrovanadate, $[V(O_2)(C_6H_4O_6)]H_2NH_4,H_2O$, forms yellowish-white, monoclinic crystals, and, when boiled in aqueous solution, yields acetone and turns green and then blue, the quinquevalent vanadium being reduced to the quadrivalent form by the citric acid. The analogous *potassium* ($+H_2O$) and *sodium* ($+H_2O$) salts form colourless, monoclinic crystals and the normal *silver citrovanadate* a white, microcrystalline powder. T. H. P.

Terpenes and Ethereal Oils. CXVIII. Transformation Products of Methylheptanone and Allied Compounds. O. Wallach (*Annalen*, 1915, **408**, 183—202).—The addition of hydrogen to β-methyl-Δ^{β}- and -Δ^{δ}-hepten-ζ-ones, when these are reduced to β-methylheptan-ζ-one by Paal's method, occurs more readily with the former than with the latter. The saturated ketone, by reduction with

sodium and moist ether, yields, in addition to the methylheptanol, a *pinacone*, $C_{16}H_{34}O_2$, m. p. 43—44°, b. p. about 300° or 170°/14 mm.

[With PAUL SCHULZE and HEINRICH GRÖPPEL.]—*β*ζ-Dimethyloctan-ζ-ol has b. p. 195·5—197°, D^{20} 0·8280, and n_D 1·4335, and the hydrocarbon prepared from it has b. p. 162—163°, D^{20} 0·7490, n_D 1·4273; Barbier (A., 1914, i, 832) gives b. p. 86—88°/10 mm., D^4 0·851, and b. p. 162° respectively for the two substances. The hydrocarbon forms a crystalline *nitrosate* and *nitrolpiperidide*, and yields *β*-methylheptan-ζ-one by oxidation with 1% potassium permanganate. Its constitution, therefore, is $CHMe_2\cdot[CH_2]_3\cdot CMe{:}CHMe$, and this is confirmed by the synthesis of the hydrocarbon by the reaction between zinc, ethyl *α*-bromopropionate and *β*-methylheptan-ζ-one, carbon dioxide and water being expelled from the resulting hydroxy-acid in the usual manner.

β-Methylheptan-ζ-one is oxidised by alkaline hypobromite to *iso*heptoic acid, and reacts with bromine (1 mol.) in ether at 0° to form *η-bromo-β-methylheptan-ζ-one*, $CHMe_2\cdot[CH_2]_3\cdot CO\cdot CH_2Br$, b. p. 94—97°/14 mm., and with an excess (2 mols.) to form the *ηη-dibromo*-compound, b. p. 139—141°/18 mm. The monobromo-compound is converted by 2% aqueous potassium hydroxide or by alcoholic sodium methoxide into *β-methylheptan-η-ol-ζ-one*, b. p. 90°/12 mm., D^{20} 0·9160, n_D 1·43196 (*semicarbazone*, m. p. 170°; *oxime*, m. p. 89°; sodium hydrogen sulphite *compound*; *osazone*, yellowish-brown leaflets, m. p. 117°), which reacts with Fehling's solution to form an unsaturated *acid* containing eight atoms of carbon, the examination of which is proceeding. The preceding dibromo-compound is converted by aqueous alkali also into an unsaturated *acid*, $C_8H_{14}O_2$, b. p. 122—123°/12 mm., D^{20} 0·938, n_D 1·4511 (*silver* salt, $C_8H_{13}O_2Ag$; *amide*, m. p. 153°), but reacts with alcoholic sodium methoxide to form an (the same?) unsaturated acid and neutral products having an odour of heptaldehyde.

[With PAUL FRY.]—*iso*Propyl Δ^{β}-butenyl ketone is reduced by the Paal and the Skita methods to iso*propyl* n-*butyl ketone*,

$$CH_3\cdot[CH_2]_3\cdot COPr^{\beta},$$

b. p. 158—159°, D^{20} 0·816, n_D 1·4113 (*semicarbazone*, m. p. 110—111°; *oxime*, b. p. 135—137°/22 mm.), which is reduced by sodium and moist ether to iso*propyl*-n-*butylcarbinol*, b. p. 167—168°, D^{21} 0·820, n_D 1·4249, and the *pinacone*, $C_{16}H_{34}O_2$, m. p. 46—47°, b. p. 170—175°/14 mm., and is oxidised to acetic and valeric acids by chromic and sulphuric acids.

[With HEINRICH GRÖPPEL.]—*iso*Propyl Δ^{β}-butenyl ketone and *iso*propyl *n*-butyl ketone react less smoothly than *β*-methyl-Δ^{β}-hepten-ζ-one and *β*-methylheptan-ζ-one with Grignard reagents, the resulting tertiary alcohols being always accompanied by hydrocarbons. The following compounds have been prepared by this method: the formulæ of the unsaturated compounds are given with reserve: *Methyl*iso*propyl*-Δ^{β}-*butenylcarbinol*, $OH\cdot CMePr^{\beta}\cdot CH_2\cdot CH{:}CHMe$, b. p. 174—177°, D^{17} 0·849, n_D 1·4486, and a *hydrocarbon*, C_9H_{16}, b. p. 146—149°; *ethyl*iso*propyl*-Δ^{β}-*butenylcarbinol*, b. p. 188—191°, D^{17} 0·850, n_D 1·4521, and a *hydrocarbon*, $C_{10}H_{18}$, b. p. 158—161°; *ethyl*iso*propylbutylcarbinol*, b. p. 191—195°, D^{20} 0·8455, n_D 1·4378, from which a *hydrocarbon*, $C_{10}H_{20}$, b. p. 155—157°, D^{20} 0·7570, n_D 1·4302, is obtained by heating with zinc chloride at 150—170°. The odour of these carbinols is

piercing and unpleasant, whilst that of the carbinols derived from β-methylhepten-ζ-ones and the corresponding saturated ketone is fragrant. C. S.

Terpenes and Ethereal Oils. CXIX. Conversion of Trimethylethylene [β-Methyl-Δ^{β}-butylene] into Trimethylcyclopentenone. O. WALLACH [with JOHANNES RECHENBERG and FRITZ RIESENER] (*Annalen*, 1915, **408**, 202—211).—Amylene nitrosate which is to be used for the preparation of ethyl amylenenitrolacetoacetate must be crystallised from acetone and kept uncovered in the air for a few days. *Methyl amylenenitrolacetoacetate*,

$$NOH{:}CMe{\cdot}CMe_2{\cdot}CHAc{\cdot}CO_2Et,$$

crystals, m. p. 145—146°, is more easily purified than the ethyl ester. Either of the esters is converted by boiling 50% potassium hydroxide into an unsaturated *ketone*, $C_8H_{12}O$ (*semicarbazone*, colourless leaflets, m. p. 199—200—210° according to the method of heating), which is reduced by Skita's method to a *ketone*, $C_8H_{14}O$, b. p. 164—167°, D^{19} 0·8829, n_D 1·4336 (*semicarbazone*, m. p. 209°; *oxime*, m. p. 105°), which is a cyclo*pentanone* and probably 1 : 1 : 4-*trimethyl*cyclo*pentan*-2-*one*, since it forms a liquid *benzylidene* derivative.

The following homologues of ethyl amylenenitrolacetoacetate have been prepared: *methyl* homologue, $NOH{:}CMe{\cdot}CMe_2{\cdot}CMeAc{\cdot}CO_2Et$, m. p. 153°; *ethyl*, m. p. 163°, and *propyl*, m. p. 166°.

When air is passed for some hours through an alcoholic solution of methyl or ethyl amylenenitrolacetoacetate and sodium ethoxide, the resulting cherry-red solution yields by acidification a *substance*, $C_{10}H_{13}O_5N$, yellowish-brown powder, decomp. 212—214°, the nature of which has not yet been ascertained. C. S.

Action of Carbon Monoxide on Organo-magnesium Compounds. (Mlle.) V. EGOROVA (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1319—1332).—Zelinski (*ibid.*, 1904, **36**, 195, 336) found that carbon monoxide does not react with organo-magnesium compounds in presence of either cuprous chloride or charcoal, but from nickel carbonyl and magnesium propyl iodide he obtained: (1) an aldehyde, the formation of which was expressed by the scheme $CO + MgRX \longrightarrow R{\cdot}\overset{\cdot\cdot}{C}{\cdot}OMgX$, this $+H_2O = R{\cdot}\overset{\cdot\cdot}{C}{\cdot}OH + MgX{\cdot}OH$ and $R{\cdot}\overset{\cdot\cdot}{C}{\cdot}OH \longrightarrow R{\cdot}CH{:}O$; (2) a substance, b. p. 140—150°, which yielded a semicarbazone, m. p. 131°, and was regarded as a ketone. In place of the aldehydes and secondary alcohols which he expected, Vinay (*Diss.*, Geneva, 1909) obtained, by the action of carbon monoxide on organo-magnesium compounds, only tertiary alcohols, trimethyl-, triphenyl-, tri-*p*-tolyl-, and tri-*o*-, tri-*m*- and tri-*p*-anisyl-carbinols, being obtained in yields of 70—75%. Vinay assumed the formula C:O for carbon monoxide and regarded its action on organo-magnesium compounds as consisting of the three stages: (1) $C{:}O + MgRX \longrightarrow R{\cdot}C{:}O{\cdot}MgX$; (2) this $+MgRX \longrightarrow CRR{:}O(MgX)_2$, which decomposes into $CR_2{:}O + MgX_2 + Mg$; (3) $CR_2{:}O + MgRX \longrightarrow CR_3{\cdot}OMgX$; this with water gives $CR_3{\cdot}OH$. Vinay concludes that Zelinski's ketone, b. p. 140—150°, is dipropyl ketone and that its formation supports the scheme just given.

The results of unpublished experiments led Grignard (A., 1913, i, 693) to assert that the action of carbon monoxide on organo-magnesium compounds is expressed by the equation: $CO + MgRX \longrightarrow R{\cdot}CO{\cdot}MgX$, but that only traces of aldehydes are formed, the reaction proceeding further, with formation of secondary alcohols:

$$R{\cdot}CO{\cdot}MgX + MgRX \longrightarrow MgX{\cdot}CR_2{\cdot}OMgX \longrightarrow CHR_2{\cdot}OH.$$

The author's investigations give the following results. The action of carbon monoxide on magnesium *tert.*-butyl chloride gives a hydroxy-ketone: $CO + MgRX \longrightarrow O{:}CR{\cdot}MgX$ and $2O{:}CR{\cdot}MgX \longrightarrow MgX{\cdot}O{\cdot}CR(MgX){\cdot}CR{:}O \longrightarrow OH{\cdot}CHR{\cdot}CR{:}O$. The action of carbon monoxide on magnesium *iso*propyl bromide gives: (1) an unsaturated hydrocarbon, resulting from the dehydration of the secondary alcohol formed according to Grignard's scheme, $OH{\cdot}CHPr^{\beta}_2 \longrightarrow CMe_2{:}CHPr^{\beta}$; (2) a hydroxy-ketonic aldehyde, resulting from successive interaction of four molecules of $O{:}CR{\cdot}CR(MgX){\cdot}OMgX$, the complex formed, $MgX{\cdot}CO{\cdot}[CR(OMgX)]_3{\cdot}CR{:}O$, giving

$$CHO{\cdot}[CR(OH)]_3{\cdot}CR{:}O$$

when treated with water. The action of carbon monoxide on magnesium *tert.*-amyl chloride gives nothing but a considerable yield of *tert.*-amyl alcohol. This could not be formed by replacement of the chlorine of the amyl chloride by hydroxyl, since the chloride was not taken in excess, and its possible formation by hydration of the amylene which is always formed is not confirmed by direct experiment. Further, oxidation of magnesium *tert.*-amyl chloride to $CMe_2Et{\cdot}OMgCl$ by means of atmospheric oxygen would require as much as 15 litres of air for the quantities of the reacting compounds employed. The formation of this alcohol may be related to the formation of a new ether according to the scheme

$$R_2O + MgR_1X \longrightarrow R_2{:}OR_1{\cdot}MgX \longrightarrow R{\cdot}O{\cdot}R_1$$

(compare Stadnikov, A., 1911, i, 435), and to the work of Späth (A., 1914, i, 1), who observed the replacement of the alkyl radicle of an organo-magnesium compound by an alkyloxy-group:

$$MgRX + R_1{\cdot}OR_1 \longrightarrow MgX{\cdot}OR_1 + RR_1.$$

γ-Hydroxy-ββεε-tetramethylhexan-δ-one, $CMe_3{\cdot}CH(OH){\cdot}CO{\cdot}CMe_3$, prepared from carbon monoxide and magnesium *tert.*-butyl chloride, forms crystals, m. p. 80—82°, and has the normal molecular weight in freezing benzene. When reduced by means of magnesium *tert.*-butyl chloride, it is converted into *ββεε-tetramethylhexan-γδ-diol*,

$$CMe_3{\cdot}CH(OH){\cdot}CH(OH){\cdot}CMe_3,$$

which forms transparent crystals, m. p. 126—127°, and exhibits normal cryoscopic behaviour in acetic acid. When oxidised by means of permanganate in acid solution, it yields: (1) *ββεε-Tetramethylhexan-γδ dione*, $CMe_3{\cdot}CO{\cdot}CO{\cdot}CMe_3$, which is a yellowish-green liquid, b. p. 170—172°, D^0 0·9537, D^{20} 0·9449, and has the normal molecular weight in freezing benzene; (2) trimethylacetic acid.

The hydrocarbon, C_7H_{14}, obtained from carbon monoxide and magnesium *iso*propyl bromide, has physical constants in good agreement with those of βδ-dimethyl-Δ^{β}-pentene. The *compound*,

$$CHMe_2{\cdot}CO{\cdot}[CPr^{\beta}(OH)]_3{\cdot}CHO,$$

also formed in this reaction, forms crystals, m. p. 113—114°, b. p. 138—145°/14 mm., has the normal molecular weight in freezing

benzene and exhibits a slight acid reaction towards litmus; when oxidised, it yields the corresponding *acid*,

$$CHMe_2\cdot CO\cdot[CPr^{\beta}(OH)]_3\cdot CO_2H.$$

T. H. P.

Comparison of the Optical Rotatory Powers of the α- and β-Forms of Certain Acetylated Derivatives of Dextrose. C. S. HUDSON and J. K. DALE (*J. Amer. Chem. Soc.*, 1915, **37**, 1264—1270).—Hudson (A., 1909, i, 135) has shown that, on certain assumptions, the molecular rotations of the α- and β-aldoses may be regarded as having the values A + B for one form and − A + B for the other, where A represents the rotation due to the end asymmetric carbon atom and B the rotation of the remainder of the structure. According to this view, the sum of the molecular rotations of the two dextrose penta-acetates should be equal to the sum of those of the two tetra-acetylmethylglucosides, but Schliephacke (A., 1911, i, 16) found that this was not the case when the rotations were measured in benzene solutions. It is now shown, however, that when the rotations are determined in chloroform, methyl alcohol, or ethyl alcohol solutions, the sums of the molecular rotations are in good agreement.

The difference between the molecular rotations of α- and β-dextrose penta-acetates is the quantity 2A which, according to the theory, should be the same value for all acetylated aldoses. In the case of the octa-acetates of cellose (Schliemann, A., 1911, i, 179), however, there is a considerable divergence from the value found in the case of the dextrose penta-acetates, and it is therefore supposed that the former compounds have not yet been obtained in a pure condition. E. G.

Biochemical Synthesis of the α-Mono-*d*-galactoside of Ethylene Glycol. ÉM. BOURQUELOT, M. BRIDEL and A. AUBRY (*Compt. rend.*, 1915, **160**, 674—676; *J. Pharm. Chim.*, 1915, [vii], **11**, 290—294).—The authors have prepared *α-ethylene glycol mono-d-galactoside*, $C_6H_{11}O_5\cdot O\cdot CH_2\cdot CH_2\cdot OH$, by the action of bottom yeast on an aqueous solution containing 50 grams of the glycol and 9 grams of galactose in 100 c.c., the mixture being left for nine months at the ordinary temperature. The isolation of the galactoside, which was somewhat difficult, was effected as follows. The mixture was heated on a boiling water-bath for twenty minutes, filtered, and to the filtrate four volumes of alcohol (95%) added and the whole filtered. The alcohol and water were distilled off from the filtrate under reduced pressure, the residue treated with alcohol and then twice the volume of ether added. The precipitate was filtered off, and from the filtrate the alcohol and ether were distilled off on the water-bath. The residue was extracted with acetone, from which solution the acetone was distilled off and this residue distilled under reduced pressure at 115° to remove any ethylene glycol. The syrupy residue which crystallised in a few days was purified by several crystallisations from alcohol. The galactose so purified crystallised in colourless needles, soluble in water and alcohol, m. p. 134°, $[\alpha]_D^{20}$ + 169·9°. In aqueous solution it was readily hydrolysed by dilute sulphuric acid and slowly by bottom yeast.

W. G.

Crystalline Lævulose Penta-acetate. C. S. HUDSON and D. H. BRAUNS (*J. Amer. Chem. Soc.*, 1915, **37**, 1283—1285).—Brauns (A., 1908, i, 320) has prepared a crystalline tetra-acetate of lævulose. The penta-acetate has now been obtained in a crystalline state for the first time.

Laevulose penta-acetate, m. p. 108—109°, can be obtained from an ethereal solution in brilliant, colourless crystals, 1 cm. long and several mm. wide; it separates from benzene in crystals containing $1C_6H_6$ and melting at 90°. It has $[\alpha]_D^{20}$ −120·9° in chloroform, and −105·5° in benzene. The compound can be quantitatively hydrolysed by shaking it at 0° with 0·1 *N*-sodium hydroxide for three and a-half hours.

E. G.

Isomeric Penta-acetates of Mannose. C. S. HUDSON and J. K. DALE (*J. Amer. Chem. Soc.*, 1915, **37**, 1280—1282).—Fischer and Oetker (A., 1914, i, 143) have described a β-penta-acetylmannose, m. p. 117·5°, and $[\alpha]_D^{20}$ −24·9° in chloroform. When this substance is heated with acetic anhydride and zinc chloride, it is converted into the crystalline *α-isomeride*, m. p. 64° (corr.), and $[\alpha]_D^{20}$ +55·0° in chloroform. The difference between the molecular rotations of the mannose penta-acetates does not agree very closely with the corresponding difference in the case of the dextrose penta-acetates, and it therefore seems probable that the change from the dextrose chain to the mannose chain may cause an alteration in the value of the rotation due to the end asymmetric carbon atom (compare Hudson, A., 1909, i, 135; Hudson and Dale, this vol., i, 501).

E. G.

Certain *cyclo*Hexylhydrazones. N. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1409—1411. Compare Kishner and Belov, A., 1911, i, 678).—Dextrose, lævulose, and arabinose do not yield crystalline *cyclo*hexylhydrazones. *Mannose* cyclo*hexylhydrazone*,

$$C_6H_{12}O_5{:}N_2H{\cdot}C_6H_{11}+H_2O,$$

forms colourless needles, m. p. 143°, $[\alpha]_D$ +2·65°. *Rhamnose* cyclo*hexylhydrazone*, $C_6H_{12}O_4{:}N_2H{\cdot}C_6H_{11}$, forms colourless needles, m. p. 123—124°, $[\alpha]_D$ +7·37°.

T. H. P.

Isomeric Octa-acetates of Lactose. C. S. HUDSON and J. M. JOHNSON (*J. Amer. Chem. Soc.*, 1915, **37**, 1270—1275).—The m. p.'s which have been recorded for lactose octa-acetate are very divergent. It has now been found that the true m. p. is about 90°, but as the fused substance is very viscous and includes bubbles of air it retains a white appearance until a temperature of about 104° is reached.

When lactose octa-acetate, m. p. 90°, is dissolved in glacial acetic acid or acetic anhydride containing a small quantity of zinc chloride, an *isomeric form* is produced, which melts sharply at 152° and crystallises in slender, felted needles. It has $[\alpha]_D^{20}$ about +54° in chloroform, +28° in benzene, and +60° in glacial acetic acid, whilst the original form, m. p. 90°, has $[\alpha]_D^{20}$ about −4·5° in chloroform, −24° in benzene, and does not exhibit any rotation in glacial acetic acid. Both forms of lactose octa-acetate yield the same bromohepta-acetyl-lactose, m. p.

139—141°, and $[\alpha]_D$ in chloroform +105°, identical with the compound described by Fischer (A., 1910, i, 717).

It is considered that the lactose octa-acetate of m. p. 152° should be regarded as the α-form, and that of m. p. 90° as the β-form.

The difference between the molecular rotations of α- and β-lactose octa-acetates in several solvents is compared with that between the molecular rotations of α- and β-dextrose penta-acetates in the same solvents, and it is found that a satisfactory agreement is obtained in acetic acid and chloroform solutions, but that divergent values are obtained in benzene solutions, thus confirming Hudson and Dale's conclusion that benzene is not a suitable solvent for such comparisons (this vol., i, 501). E. G.

Isomeric α- and β-Octa-acetates of Maltose and of Cellose. C. S. Hudson and J. M. Johnson (*J. Amer. Chem. Soc.*, 1915, **37**, 1276—1280).—The method by which the authors obtained α-lactose octa-acetate (preceding abstract) has now been applied to maltose octa-acetate. *α-Maltose octa-acetate*, m. p. 125° (corr.), has thus been obtained in a crystalline form; it has $[\alpha]_D^{20}$ about +122° in chloroform, +124° in benzene or in acetic acid, and +121° in methyl alcohol. The β-form, m. p. 159—160° (corr.), has $[\alpha]_D^{20}$ about +63° in chloroform, +75° in benzene, and +56° in acetic acid.

Hudson and Dale (this vol., i, 501) have pointed out that the difference between the recorded molecular rotations of the two isomeric octa-acetates of cellose does not agree with the corresponding difference for the two dextrose penta-acetates. A study has therefore been made of the cellose octa-acetates. The α-form, m. p. 229·5° (corr.), has $[\alpha]_D^{20}$ +41·9° in chloroform, and the β-form, m. p. 202° (corr.), has $[\alpha]_D^{20}$ about −14·6° in the same solvent. The difference between the molecular rotations of these isomerides agrees well with that for the α- and β-dextrose penta-acetates and that for the α- and β-lactose octa-acetates, the value of this difference being a measure of the rotatory power of the end asymmetric carbon atom which is common to all the acetylated aldoses (compare Hudson, A., 1909, i, 135).

E. G.

***epi*Fucose.** Emil Votoček and J. Červený (*Ber.*, 1915, **48**, 658—660).—The number of the aldehydic methylpentoses has been increased by *epi*fucose (II), the isomeride of fucose (I). The lactone

(I.) $OH\cdot CHMe\cdot\overset{H}{\overset{|}{C}}\!\!-\!\!\overset{H}{\overset{|}{C}}\!\!-\!\!\overset{OH}{\overset{|}{C}}\cdot CHO$ (II.) $OH\cdot CHMe\cdot\overset{H}{\overset{|}{C}}\!\!-\!\!\overset{H}{\overset{|}{C}}\!\!-\!\!\overset{H}{\overset{|}{C}}\cdot CHO$

$\quad\quad\quad

phenylhydrazone and *p*-bromophenylhydrazone were isolated, identical with the derivatives of fucose.

The author states that his expression, "epimerism," has been adopted in Meyer and Jacobson's new text-book, and by others, although it was not favoured by E. Fischer. J. C. W.

Action of Nitrous Acid on the Amines. PAÑCHĀNAN NEOGI (*Chem. News*, 1915, **111**, 255).—Mainly a re-statement of work of which an account has already been published (T., 1914, **105**, 1270). The action of nitrous acid on amines other than purely aromatic amines is one of simple neutralisation, the resulting amine nitrites decomposing on heating into alcohol and nitrogen in the case of primary amines, nitroso-compounds with secondary amines, and free base, nitrate, and nitric oxide with tertiary amines. G. F. M.

The Addition of Aliphatic Amines to Metallic Salts. WALTER PETERS (*Zeitsch. anorg. Chem.*, 1914, **89**, 191—209. Compare A., 1913, ii, 42).—In accordance with its higher constant of affinity, methylamine has a greater additive power than ammonia. Thus potassium platinichloride does not combine with ammonia, but absorbs 12 mols. of methylamine, whilst sodium platinichloride combines with $6NH_3$ and $12NH_2Me$. Copper and zinc platinithiocyanates combine with $15NH_3$ or $24NH_2Me$. On the other hand, only cuprous chloride and silver chloride and bromide show slightly less combining power for methylamine than ammonia.

Dimethylamine, in spite of its greater constant of affinity, has a lower additive power than methylamine, possibly owing to steric hindrance. Potassium platinichloride combines with $6NHMe_2$, and the copper salt with $12NHMe_2$, but $18NH_2Me$. The platinithiocyanates of copper and zinc combine with $18NHMe_2$.

The salts examined, with the exception of copper platinicyanide and platinithiocyanate, which combine with $2NMe_3$ and $4NMe_3$ respectively, are indifferent towards trimethylamine. The behaviour of twenty-nine salts towards the mono- and di-amines is tabulated. In a few cases reduction of the metallic salt takes place.

[With MARGARETE MÜLLER.]—Cuproso-cupric cyanide yields in aqueous solution only the crystalline compounds, $Cu_3(CN)_4,2NHMe_2$ and $Cu_3(CN)_4,2NMe_3$, the products obtained by Litterscheid (A., 1904, i, 301) being impure.

Phosphine does not combine with the salts examined. The supposed combination with aluminium chloride is explained by condensation to form solid hydrogen phosphide.

The ammoniate of mercuric cyanide has a higher vapour pressure than that of mercuric bromide, but lower than that of mercuric iodide. C. H. D.

Hexabromoselenates [Selenibromides]. A. GUTBIER and F. ENGEROFF (*Zeitsch. anorg. Chem.*, 1914, **89**, 307—312. Compare A., 1912, i, 241; ii, 343).—The following further selenibromides have been prepared: *Tetramethylammonium*, $(NMe_4)_2SeBr_6$; *tri-* and *tetraethylammonium*, iso*propylammonium*, *dipropylammonium*, *diisobutylam-*

monium, pyridinium, α- and *β-picolinium.* Whilst some of these salts dissolve in water to a clear solution, others are decomposed with the formation of colloidal selenium. C. H. D.

Hexabromo-osmates [Osmibromides]. A. GUTBIER and L. MEHLER [with N. PFANNER, and O. EDELHÄUSER] (*Zeitsch. anorg. Chem.*, 1914, **89**, 313—332. Compare A., 1912, i, 241; ii, 343).—The compounds are prepared in hydrobromic acid solution, and either crystallise immediately or are obtained by spontaneous evaporation and recrystallisation. They are stable in air, but more or less decomposed by solvents, with the exception of hydrobromic acid. The following salts have been obtained:

Methylammonium osmibromide, $(NH_3Me)_2OsBr_6$; *di-, tri-,* and *tetramethylammonium, benzylidenemethylammonium, benzylmethylammonium, mono-, di-, tri-* and *tetra-ethylammonium, nitrosodiethylammonium, benzylidene-ethylammonium, benzylethylammonium, propyl-,* iso*propyl-, di-* and *tri-propylammonium; butyl-* and *mono-, di-* and *tri-*iso*butylammonium; allylammonium, mono-, di-,* and *tri-*iso*amylammonium; ethylene-* and *propylene-diammonium; guanidinium, triphenylguanidinium, anilinium, mono-* and *di-methyl-* and *ethyl-anilinium;* iso*amyl-, benzylidene-* and *benzyl-anilinium; benzylmethyl-* and *benzylethyl-anilinium;* m- and p-*chloro-* and 2 : 4-*dichloro-anilinium;* o-, m-, and p-*bromoanilinium; benzylammonium, tribenzylammonium,* o-, m-, and p-*toluidinium; dimethyl-*o- and -p-*toluidinium;* 2:4-, 3:4-, and 4:5-*xylidinium; ψ-cumidinium,* m-*phenylenediammonium,* 2 : 4- and 3 : 4-*tolylenediammonium;* o- and p-*anisidinium* and *-phenetidinium; pyridinium, α-* and *β-picolinium; lutidinium, collidinium, piperidinium,* and iso*quinolinium.* C. H. D.

Hexachloro-osmates [Osmichlorides]. A. GUTBIER and L. MEHLER (*Zeitsch. anorg. Chem.*, 1914, **89**, 333—339. Compare A., 1911, i, 191, and preceding abstract).—The osmichlorides may be recrystallised well from hydrochloric acid, and are stable in air. The following are described: *Tetramethylammonium, tri-* and *tetra-ethylammonium; tripropylammonium, di-* and *tri-*iso*butylammonium; allylammonium, di-* and *tri-*iso*amylammonium; guanidinium, triphenylguanidinium,* iso*amylanilinium,* m-*chloroanilinium,* o-, m-, and p-*bromoanilinium; tribenzylammonium; ψ-cumidinium, β-picolinium, lutidinium; collidinium, piperidinium,* and iso*quinolinium.* C. H. D.

Hexachloro-iridates [Iridichlorides]. A. GUTBIER and BERTA OTTENSTEIN (*Zeitsch. anorg. Chem.*, 1914, **89**, 344—351. Compare A., 1910, i, 97).—The iridichlorides are dark red, and dissolve in water to dark solutions, which become yellow on dilution and soon decompose. The solutions in hydrochloric acid are very stable. The following salts are described: *Tetramethylammonium,* $(NMe_4)_2IrCl_6$; *benzylidenemethylammonium, benzylmethylammonium, tetraethylammonium, benzylidene-ethylammonium, benzylethylammonium, tripropylammonium, tri*iso*butylammonium, allylammonium, di-* and *tri-*iso*amylammonium; guanidinium, triphenylguanidinium, benzylideneanilinium,* p-*chloroanilinium,* m- and p-*bromoanilinium; tribenzyl-*

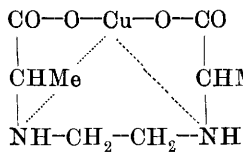
ammonium, *dimethyl-o-toluidinium*, *ψ-cumidinium*, *β-picolinium*, *lutidinium*, *piperidinium*, and iso*quinolinium*. C. H. D.

Preparation of Glucosamic Acid. HANS PRINGSHEIM and GERHARD RUSCHMANN (*Ber.*, 1915, **48**, 680—682).—Glucosamine hydrochloride can be oxidised to glucosamic acid in a few minutes instead of weeks (compare Fischer and Tiemann, A., 1894, i, 167) by warming the solution with yellow mercuric oxide, precipitating the mercury from the halogen-free filtrate of the mercury salt by hydrogen sulphide, and evaporating the clear liquid under reduced pressure. The mother liquors from the first crystallisation of the pure acid may be precipitated by alcohol. The total yield is about 54%. J. C. W.

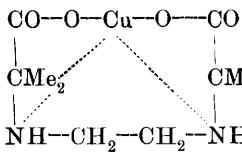
Poly-membered Rings in the Copper Salts of Bisimino-acids. N. A. SCHLESINGER (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1575—1579).—The copper salt of αα′-ethylenebisiminopropionic acid, $C_8H_{14}O_4N_2Cu$, and that of αα′-ethylenebisimino*iso*butyric acid,

$$C_{10}H_{18}O_4N_2Cu + 4H_2O$$

(compare A., 1912, i, 555), are shown by cryoscopic determinations in water and by conductivity measurements to be completely non-ionised and, therefore, of an internal-complex character. Their formulæ,



and



show that they contain an 11-membered ring. The relation of these salts, which furnish additional examples of stable, poly-membered, heterocyclic systems (compare Autenrieth and Geyer, A., 1909, i, 6; Autenrieth and Beuttel, A., 1910, i, 60, 61), to Baeyer's tension theory is discussed. T. H. P.

αα′-Ethylenebisimino-acids. N. A. SCHLESINGER (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1579—1597, and *Ber.*, 1914, **47**, 2406—2417).—Most of the results given in this paper have been published previously (A., 1911, i, 427; 1912, i, 555), the new matter being as follows.

αα′-*Ethylenedi-iminodi*iso*butyronitrile*, $C_2H_4(NH\cdot CMe_2\cdot CN)_2$, which forms transparent, oblique-angled plates, m. p. 55—56°, and its *sulphate*, $C_{10}H_{18}N_4,H_2SO_4$, and *methyl* αα′-*ethylenedi-iminodi*iso*butyrate*, m. p. 39—40°, b. p. 170°/25 mm., and its *hydrochloride*,

$$C_{12}H_{24}O_4N_2,2HCl,$$

have been prepared.

αα′-*Ethylenedi-iminodioctonitrile hydrochloride*,

$$C_2H_4\{NH\cdot CH(CN)\cdot[CH_2]_5\cdot CH_3\}_2,2HCl,$$

prepared from ethylenediamine hydrochloride, potassium cyanide, and heptaldehyde, yields on hydrolysis: (1) the corresponding *amide*, $C_2H_4\{NH\cdot CH(CO\cdot NH_2)\cdot[CH_2]_5\cdot CH_3\}_2$, m. p. 175·6—176·6° (decomp.); the *hydrochloride* (+2HCl) was analysed; (2) αα′-*ethylenedi-iminodi-*

octoic acid, $C_2H_4\{NH\cdot CH(CO_2H)\cdot[CH_2]_5\cdot CH_3\}_2$, the *hydrochloride* (+2HCl) of which decomposes when dried until of constant weight.

2 : 3-*Diphenylpiperazine*-2 : 3-*dicarboxynitrile*,

$$NH<\begin{matrix}CPh(CN)\cdot CPh(CN)\\ CH_2\text{————}CH_2\end{matrix}>NH,$$

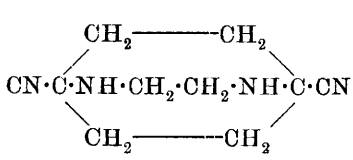
obtained by the interaction of ethylenediamine hydrochloride, potassium cyanide, and benzil, has m. p. 123° (decomp.), and forms crystalline compounds with 1Et·OH, m. p. 248—249°, and with 1Me·OH.

2 : 3-*Diphenylpiperazine*-2 : 3-*dicarboxylic acid*,

$$NH<\begin{matrix}CPh(CO_2H)\cdot CPh(CO_2H)\\ CH_2\text{————}CH_2\end{matrix}>NH,$$

was not obtained crystalline; its *hydrochloride* (+2HCl) and its *copper* salt were analysed.

The interaction of ethylenediamine hydrochloride, potassium cyanide, and *cyclo*hexane-1 : 4-dione yields the *bicyclic bisiminonitrile* (annexed formula), which decomposes completely at about 110° and cannot be converted into the corresponding dicarboxylic acid by means of fuming hydrochloric acid, since it undergoes decomposition into its components, the diamine, the diketone, and hydrogen cyanide; with concentrated sulphuric acid the nitrile appears to give the acid, but only in very minute yield.



T. H. P.

Compounds of Vanadicarbamide. G. A. Barbieri (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 435—438).—The analogy between tervalent vanadium, iron and chromium extends to the formation of compounds of vanadicarbamide, similar to those of chromicarbamide and ferricarbamide (compare A., 1913, i, 959). These compounds have the general formula $VX_3,6CO(NH_2)_2$, and are mostly bluish-green, but, as is the case with chromicarbamide and ferricarbamide, the periodide is reddish-brown. The dichromate and permanganate cannot be prepared, since tervalent vanadium is oxidised by chromic or permanganic acid, even in presence of carbamide. Vanadicarbamide compounds are regarded as aquo-salts derived by substitution of six molecules of water by six molecules of carbamide, which remain united to the central metallic atom by means of the secondary valencies of the oxygen atom, thus: $\left[V'''\left(OC\begin{matrix}NH_2\\ NH_2\end{matrix}\right)_6\right]X_3$. This replacement of water by carbamide takes place, as with ferric salts, in the cold, whilst with chromic salts it is possible only in the hot (compare Pfeiffer, A., 1903, i, 612), the hydrated ions of vanadium and iron being less stable than those of chromium. Further, the complex, $[V(CO\cdot N_2H_4)_6]$, like the corresponding ferric complex, is far less stable than $[Cr(CO\cdot N_2H_4)_6]$, and exists in solution only in presence of a large excess of carbamide.

Vanadicarbamide perchlorate, $[V(CO\cdot N_2H_4)_6](ClO_4)_3$, when dry, is stable in the air and does not absorb moisture or undergo oxidation.

It gives a green solution, which rapidly becomes yellowish-brown owing to hydrolysis, the green colour being restored by addition of an acid. The *bromide*, $[V(CO\cdot N_2H_4)_6]Br_3,3H_2O$, forms a pale, greenish-blue, crystalline powder, the *iodide*, $[V(CO\cdot N_2H_4)_6]I_3$, greenish-blue, acicular crystals, and the *sulphate periodide*, $[V(CO\cdot N_2H_4)_6]SO_4I,I_2$, in which the vanadium doubtless possesses a higher valency, reddish-brown, microscopic needles. T. H. P.

Mechanism of the Strecker Reaction. G. L. STADNIKOV (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1201—1215).—The author criticises Snesarev's views and certain of his experimental results (A., 1914, i, 670, 671), and reaffirms his own statement that the formation of iminonitrile in the Strecker synthesis of α-aminonitriles is due to the interaction of the latter with hydroxy-nitriles (A., 1907, i, 393, 1015). T. H. P.

Compounds of Chromates and Dichromates with Mercuric Cyanide. D. STRÖMHOLM (*Zeitsch. anorg. Chem.*, 1914, **90**, 361—369. Compare A., 1913, i, 347).—The following crystalline compounds have been obtained: $2Rb_2CrO_4,3Hg(CN)_2,2H_2O$; $Cs_2CrO_4,2Hg(CN)_2,H_2O$; $2(NH_4)_2CrO_4,3Hg(CN)_2,2H_2O$; $(NH_3Me)_2CrO_4,2Hg(CN)_2$; $(NH_2Me_2)_2CrO_4,2Hg(CN)_2,H_2O$ and possibly a second compound; $(NHMe_3)_2CrO_4,2Hg(CN)_2,H_2O$; $(NMe_4)_2CrO_4,2Hg(CN)_2,H_2O$; $2(NH_3Et)_2CrO_4,Hg(CN)_2,H_2O$; $(NH_2Et_2)_2CrO_4,2Hg(CN)_2$; $(SMe_3)_2CrO_4,2Hg(CN)_2,H_2O$.

The corresponding sodium, triethylammonium and tetraethylammonium salts have not been prepared in a pure state.

The following dichromate compounds are also crystalline: $Cs_2Cr_2O_7,Hg(CN)_2$; $(NH_3Me)_2Cr_2O_7,Hg(CN)_2$; $(NHMe_3)_2Cr_2O_7,2Hg(CN)_2$; $(NMe_4)_2Cr_2O_7,2Hg(CN)_2,H_2O$; $(NEt_4)_2Cr_2O_7,2Hg(CN)_2$; $(SMe_3)_2Cr_2O_7,Hg(CN)_2$; $(SMe_3)_2Cr_2O_7,2Hg(CN)_2$.

C. H. D.

Ferrocyanides and Mercuric Cyanide. II. D. STRÖMHOLM (*Zeitsch. anorg. Chem.*, 1914, **90**, 370. Compare A., 1914, i, 24).—Two additional compounds are described, $Cs_4Fe(CN)_6,3Hg(CN)_2$ and $(NHMe_3)_4Fe(CN)_6,3Hg(CN)_2$.

C. H. D.

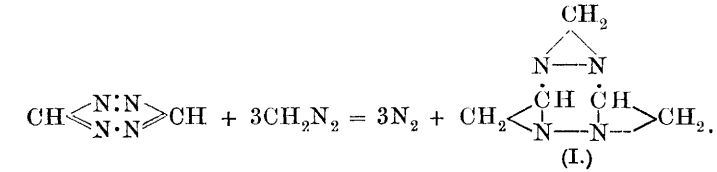
Formation of Carbonylferrocyanides, and Decomposition of Sodium Nitroprusside by Sulphuric Acid. JOSÉ GIRAL PEREIRA (*Anal. Fis. Quim.*, 1915, **13**, 166—176. Compare this vol., i, 389).—The interaction of sodium nitroprusside and similar substances with concentrated sulphuric acid takes place partly in accordance with the equation: $2Na_2(NO)Fe(CN)_5 + 7H_2SO_4 + 5H_2O = 2H(NO)SO_4 + NaHSO_4 + NH_4HSO_4 + 2(NH_4)_2SO_4 + FeSO_4 + 5CO + Na_3Fe(CN)_5$. The pentacyanide formed is then attacked by the carbon monoxide:

$Na_3Fe(CN)_5 + CO = Na_3(CO)Fe(CN)_5$. The carbonylferrocyanide reacts with the ferrous sulphate:

$$2Na_3(CO)Fe(CN)_5 + 3FeSO_4 = Fe_3'''[(CO)Fe(CN)_5]_2 + 3Na_2SO_4.$$

The violet coloration produced is due to the formation of this ferric carbonylferrocyanide. The method affords an accurate and rapid method for the formation of compounds of this type. A. J. W.

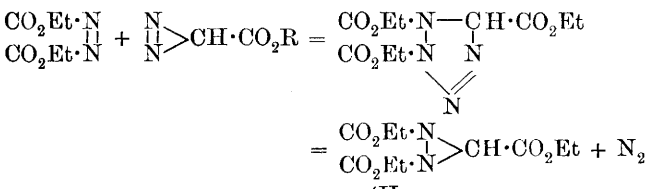
Some Derivatives of the Genuine Hydraziacetic Acid. ERNST MÜLLER (*Ber.*, 1914, **47**, 3001—3023).—When 1 : 2 : 4 : 5-tetrazine is treated with diazomethane, instead of taking up two methylene groups to form a dimethyltetrazine with the elimination of 2 mols. of nitrogen, it takes up three groups at the three double linkings with the evolution of 3 mols. of nitrogen, yielding *trimethylenetetrazine* (I), which is pale brown and not red like the typical tetrazines; thus:



(I.)

The compound is hydrolysed by dilute sulphuric acid to formaldehyde and hydrazine.

This addition of methylene groups has been studied further in the case of ethyl azodicarboxylate, which is shown to react with ethyl diazoacetate, in alcoholic solution, to give a derivative of the true hydraziacetic acid, thus:



(II.

The reaction is therefore analogous to the formation of ethyl trimethylenetricarboxylate from ethyl fumarate and ethyl diazoacetate (Buchner and Witter, A., 1895, i, 269), although, in the present case, the hypothetical intermediate compound could not be characterised.

The constitution of the above ethyl hydrazimethanetricarboxylate (II) was definitely ascertained by hydrolysis. A number of hydrazine derivatives which were at one time regarded as hydrazi-compounds have since been recognised as simple hydrazones (compare Forster and Cardwell, T., 1913, **103**, 861), and what was originally called hydraziacetic acid has been shown to be the hydrazone of glyoxylic acid (Darapsky, A., 1912, i, 543). The chief difference between the present genuine hydrazimethane derivatives and the wrongly so-called examples is that they are very much more difficult to hydrolyse by acids.

Attempts have naturally been made to prepare the true hydraziacetic

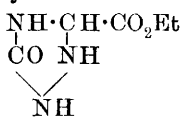
acid itself and also the very interesting hydrazimethane, $CH_2<\begin{matrix}NH\\NH\end{matrix}$, but as yet without success.

If ethyl diazoacetate and ethyl azodicarboxylate are allowed to react without alcohol as a diluent, violent decomposition ensues unless the temperature is not allowed to rise above 120°. Even then, the product is quite different from the above tri-ester. It has the formula $C_5H_9O_3N_3$, and yields hydrazine, ammonia and glyoxylic acid on hydrolysis. Of four possible formulæ for such a compound, the important ones to consider were those of the semicarbazone of ethyl glyoxylate (III), and the carbethoxyhydrazone of glyoxylamide (IV).

$NH_2\cdot CO\cdot NH\cdot N{:}CH\cdot CO_2Et$ (III.) $\qquad$ $NH_2\cdot CO\cdot CH{:}N\cdot NH\cdot CO_2Et$ (IV.)

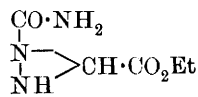
These were synthesised and the above compound was shown to be identical with IV.

Well-defined amides of hydrazimethanetricarboxylic acid could not be obtained by the action of ammonia on the above ester. Ethyl diazoacetate was therefore made to react with azodicarbonamide, but the product was, again, a compound of the formula $C_5H_9O_3N_3$. It was hydrolysed by concentrated hydrochloric acid in a sealed tube to alcohol, carbon dioxide, ammonia, hydrazine and glyoxylic acid, but the semicarbazone of glyoxylic acid was isolated when dilute sulphuric acid was used, and the semicarbazone of ethyl glyoxylate when the substance was boiled with water for some time. The compound may be represented by either of the remaining alternatives to III and IV, namely:



(V.)

or



(VI.

the latter being regarded as the more probable, for the substance is unstable, quite neutral, and cannot be oxidised to anything like a triazolone.

Ethereal solutions of ethyl azodicarboxylate and diazomethane were mixed and submitted to distillation after the vigorous evolution of nitrogen had ceased. The product, *ethyl hydrazimethanedicarboxylate*, $CH_2<\begin{matrix}N\cdot CO_2Et\\N\cdot CO_2Et\end{matrix}$, was a colourless oil, b. p. 168°/14 mm., 113°/0·03 mm., which gave formaldehyde on hydrolysis, and ethyl azodicarboxylate when treated with concentrated nitric acid. It was probably contaminated with ethyl hydrazinedicarboxylate which has the same b. p.

A mixture of ethyl azodicarboxylate and ethyl diazoacetate in alcohol was carefully manipulated until the evolution of nitrogen had ceased and then distilled. *Ethyl hydrazimethanetricarboxylate* (II) distilled at 190—191°/14 mm. as a viscid oil, which crystallised from alcohol in colourless tablets, m. p. 61°. It was hydrolysed by various agents and the products were isolated; concentrated hydrochloric acid in a sealed tube gave carbon dioxide, hydrazine, ammonia and oxalic acid; dilute sodium hydroxide gave glyoxylic acid; fuming nitric

acid gave ethyl azodicarboxylate (and this, azodicarbonamide); 2*N*-sulphuric acid gave ethyl hydrazinedicarboxylate and ethyl glyoxylate.

Azodibenzoyl was also treated with ethyl diazoacetate in alcohol, and the residue, after evaporation under reduced pressure, was extracted by ether. This left a small amount of insoluble tribenzoylhydrazine (Stollé and Benrath, A., 1904, i, 935) and dissolved *ethyl dibenzoylhydraziacetate*, $\begin{matrix}\mathrm{NBz}\\ |\\ \mathrm{NBz}\end{matrix}\!\!>\!\mathrm{CH}\cdot\mathrm{CO_2Et}$, which crystallised in colourless tablets, m. p. 70°. It is very stable towards dilute acids. The same products were obtained, in this case, in the absence of alcohol, an explosion being prevented by cooling in a freezing mixture.

Equimolecular proportions of ethyl diazoacetate and ethyl azodicarboxylate were mixed and the reaction so controlled that the temperature was kept between 100° and 120°. The main bulk of the product, which distilled at 183—184°/15 mm., was dissolved by a concentrated solution of ammonia, which deposited, on cooling, the *carbethoxyhydrazone* of *glyoxylamide* (IV), in colourless tablets (or bundles of needles from water), m. p. 239—241°. The mother liquor was evaporated and the residue, after some trouble, was separated into a small amount of ethyl hydrazinedicarboxylate and a trace of the compound IV. The latter was synthesised as follows; ethyl glyoxylate and ethyl hydrazinecarboxylate, $\mathrm{NH_2\cdot NH\cdot CO_2Et}$, were mixed in water, when the *carbethoxyhydrazone* of *ethyl glyoxylate*,

$$\mathrm{CO_2Et\cdot NH\cdot N{:}CH\cdot CO_2Et},$$

soon separated as a white substance, m. p. 100°. This gave the above amide when dissolved in ammonia.

An alcoholic solution of ethyl diazoacetate was mixed with finely powdered azodicarbonamide and heated on the water-bath for thirty hours. The filtrate from a small residue deposited the above *compound* VI, on cooling, in slender needles, m. p. 174—175°. In order to compare it, and the compound IV, with the semicarbazone of ethyl glyoxylate, the latter was prepared by shaking ethyl glyoxylate alcoholate with semicarbazide hydrochloride and potassium acetate in water. It has m. p. 210—212° (compare Baily and Read, A., 1914, i, 1055). It was once obtained when the above reaction between ethyl diazoacetate and azodicarbonamide proceeded at a higher temperature, owing to the failure of a reflux condenser. J. C. W.

A Lecture on Fifty Years of Benzene Research. A. F. Holleman (*Chem. Weekblad*, 1915, **12**, 440—465).—An epitome of work on the constitution of benzene from the time of Kekulé to the present day. A. J. W.

Tetranitromethane as a Reagent for the Structure of the Molecule. Or. Filipov (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1199—1201).—Tetranitromethane gives a yellow coloration with ethyl*cyclo*propane or acetyl*cyclo*propane, but not with methyl*cyclo*butane, the tertiary alcohol from Gustavson's hydrocarbon or the corresponding glycol or dibromo-derivative, methyl*cyclo*butene, methylene*cyclo*butane or 1 : 1 : 2 : 2-tetramethyl-3 : 4-di*iso*propyl*cyclo*butane.

These results contradict Ostromisslenski's statement to the effect that *cyclo*butane derivatives give colorations with tetranitromethane ("Caoutchouc and its Analogues," Moscow, 1913, 42), and invalidate the same author's exclusion of Harries' formula for caoutchouc bromide, as well as the structure given by him for the hydrocarbon obtained from sorbic acid. It would appear from the author's results that this reagent serves as a means of distinguishing between three- and four-membered rings. T. H. P.

Structure of Gustavson's Hydrocarbons, Obtained from Pentaerythritol. Or. Filipov (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1141—1199).—The author gives a critical résumé of previous investigations on these hydrocarbons (compare Gustavson, A., 1896, i, 669; Gustavson and Popper, A., 1898, i, 6; Gustavson and Bulatov, A., 1898, i, 13; Ipatiev and Tichocki, *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 760; Fecht, A., 1907, i, 906; Östling, T., 1912, **101**, 457; Zelinski, A., 1913, i, 254; Demjanov and Dojarenko, A., 1913, i, 451; Mereshkovski, A., 1914, i, 923).

Details are also given of the author's work, which includes transformation of pentaerythritol into the corresponding tetrabromo-derivative, conversion of this into Gustavson's hydrocarbons, separation, oxidation and reduction of the latter, and syntheses of ethyl*cyclo*propane and methyl*cyclo*butane. From the results obtained the conclusion is drawn that Gustavson's hydrocarbons are methylene*cyclo*butane and 1-methyl-Δ^1-*cyclo*butene, the formation of the latter from the former being expressed by the scheme:

$$CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>C{:}CH_2 + HX \longrightarrow$$

$$CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>CMeX \longrightarrow CH_2<\begin{matrix}CH_2\\CH\end{matrix}>CMe$$

(compare Favorski and Batalin, this vol., i, 390). T. H. P.

The Saturated Hydrocarbons of Vacuum Coal Tar Oil. Amé Pictet and Maurice Bouvier (*Compt. rend.*, 1915, **160**, 629—631; *Ber.*, 1915, **48**, 926—933).—A continuation of work already published on this subject (A., 1914, i, 155), the authors having isolated four new saturated hydrocarbons. The method, as already described (*loc. cit.*), has been used, except that liquid sulphur dioxide has been adopted instead of fuming sulphuric acid as solvent for the unsaturated hydrocarbons. All these saturated hydrocarbons have the general formula C_nH_{2n}, and the six now isolated from the vacuum oil have the following physical constants.

Formula	B. p. /730 mm.	D.	n_D.
C_9H_{18}	135—137°	0·7590 at 20°	1·4212 at 20°
$C_{10}H_{20}$	160—161°	0·7680 at 20°	1·4272 at 20°
$C_{10}H_{20}$	172—174°	0·7765 at 23°	1·4196 at 23°
$C_{11}H_{22}$	189—191°	0·7838 at 22°	1·4234 at 22°
$C_{12}H_{24}$	211—213°	0·7862 at 21°	1·4293 at 21°
$C_{13}H_{26}$	227—229°	0·7953 at 20°	1·4379 at 20°

The values of these physical constants are in close accord with

those obtained by Mabery for saturated hydrocarbons having the same constitutions and derived from Galician and Californian petroleum. The authors consider the hydrocarbon C_9H_{18} to be hexahydromesitylene [1 : 3 : 5-trimethyl*cyclo*hexane], since with nitric acid it yields dinitromesitylene.

By continuing the distillation of the vacuum oil (which at ordinary pressure decomposes at 240°) further at 15 mm. pressure the authors have obtained a fraction which solidifies, giving colourless needles, m. p. 62—63°, D^{25} 0·9128, and having the constitution $C_{30}H_{60}$. This hydrocarbon can also be obtained by extracting the original coal with boiling benzene, and it has also been isolated from the paraffin wax of Galician petroleum. It is identical with the melene obtained by Brodie in the dry distillation of beeswax (compare *Annalen*, 1849 **71**, 156). W. G.

Action of Nitric Acid on Saturated Compounds. S. S. Nametkin and (Mlle.) A. K. Rushenceva (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1540—1544).—The action of nitric acid on ω-nitromethyl*cyclo*hexane (hexahydrophenylnitromethane) yields principally adipic acid (compare Nametkin, A., 1910, i, 830). This change may take place in either of two ways : (1) The *cyclo*hexanealdehyde formed by Nef's reaction from the salt of the *iso*nitro-compound is first oxidised to *cyclo*hexanecarboxylic acid, which then undergoes nitration at the tertiary hydrogen atom nearest to the carboxyl group; the α-nitro-acid thus formed immediately loses carbon dioxide, and the process is completed according to the general scheme for the action of nitric acid at a methylene group (A., 1909, i, 93, 372). (2) The initial action of the nitric acid may take place, not at the aldehydic group of the *cyclo*hexanealdehyde, but at one of the neighbouring groups, so that, in the conversion of the aldehyde into adipic acid, the formation of *cyclo*hexanecarboxylic acid is avoided. In order to decide this question, the authors have investigated the action of nitric acid on a number of compounds, with the following results.

*cyclo*Hexylcarbinol yields adipic acid; *cyclo*pentylcarbinol, principally glutaric acid, with a very small portion of succinic acid; *cyclo*butylcarbinol, succinic acid; *cyclo*hexanealdehyde, adipic acid; *cyclo*pentanealdehyde, glutaric acid; *cyclo*hexane-, *cyclo*pentane- and *cyclo*butane-carboxylic acids, practically unattacked, no trace of adipic, glutaric and succinic acids respectively being obtained.

Thus, all the alicyclic carbinols and aldehydes examined react readily with nitric acid, the principal products being dibasic acids with the same number of carbon atoms in the molecule as take part in the formation of the ring. This rule is in agreement with what was previously established in the oxidation by nitric acid of alicyclic hydrocarbons at a methyl group (A., 1910, i, 830; 1912, i, 175). With the corresponding monobasic or naphthenic acids, the reaction is extremely slow and, even after prolonged boiling, no trace of the corresponding dibasic acid is obtained. These results support the second of the two schemes given above for the reaction.

In general it may be stated that, on oxidation of alicyclic compounds by nitric acid, with formation of the corresponding dibasic acids,

resolution of the cyclic system at the side group takes place without formation of the naphthenic acids. T. H. P.

Steric Hindrance of Chemical Reactions. II. Dimesityl Compounds. F. WENZEL [with RICHARD KUGEL] (*Monatsh.*, 1914, **35**, 953—963).—Dimesitylmethane and dimesitylethane may be readily prepared by the condensation of methylene dibromide and ethylene dibromide with mesitylene in the presence of aluminium chloride. Attempts to prepare dimesitylpropane from trimethylene dibromide in a similar manner were unsuccessful.

Dimesitylmethane crystallises in small, white needles, m. p. 135°, (Baeyer, this Journ., 1873, 501, gives 130°). It is best prepared by the interaction of mesitylene and chloromethyl acetate in the presence of aluminium chloride. On treatment with bromine in glacial acetic acid solution it yields a *tetrabromo*-derivative, crystallising in needles, m. p. 223—225°.

3 : 5 : 3′ : 5′-*Tetranitro*-2 : 2′ :4 : 4′ : 6 : 6′-*hexamethylbenzophenoneoxime*, $OH\cdot N{:}C[C_6Me_3(NO_2)_2]_2$, prepared by heating dimesitylmethane with a mixture of concentrated sulphuric and nitric acids on the water-bath, forms slender, prismatic needles, which become brown at 220°, m. p. 225—230°; nitration at the ordinary temperature yields *tetranitrodimesitylmethane*, $CH_2[C_6Me_3(NO_2)_2]_2$, decomposing at 230° with previous browning at 215°.

A *mononitrodimesitylmethane*, crystallising in needles, m. p. 220—225°, is obtained by nitrating dimesitylmethane with sulphuric acid and ammonium nitrate in glacial acetic acid solution at the ordinary temperature in the presence of carbamide.

s-*Dimesitylethane*, $C_6H_2Me_3\cdot CH_2\cdot CH_2\cdot C_6H_2Me_3$, prepared from mesitylene and ethylene dibromide, crystallises in spherical aggregates of slender needles, m. p. 117—118°, and yields a *tetrabromo*-derivative, small, white needles, m. p. 178—180°. F. B.

Steric Hindrance of Chemical Reactions. IV. Di-ψ-cumylmethane. F. WENZEL [and GUSTAV BRADA] (*Monatsh.*, 1914, **35**, 973—986).—ψ-Cumene differs from the isomeric hydrocarbon, mesitylene, in that it undergoes condensation with methylene dichloride in the presence of aluminium chloride with much greater difficulty. The di-ψ-cumylmethane thus obtained in small yield is readily prepared by the condensation of ψ-cumene with methylal by means of sulphuric acid in glacial acetic acid solution at the ordinary temperature. Attempts to prepare di-ψ-cumyl ketone by oxidising di-ψ-cumylmethane were unsuccessful, the hydrocarbon being either recovered unchanged or partly converted into acids owing to the oxidation of the methyl groups.

Di-ψ-cumylmethane (2 : 4 : 5 : 2′ : 4′ : 5′-*hexamethyldiphenylmethane*), $CH_2(C_6H_2Me_3)_2$, has b. p. 189—190°/12 mm., and crystallises in slender, lustrous, snow-white needles, m. p. 99° with previous softening at 95°. On treatment with fuming nitric and concentrated sulphuric acids it is converted into *tetranitrodi-ψ-cumylketoxime* [3 : 6 : 3′ : 6′-*tetranitro*-2 : 4 : 5 : 2′ : 4′ : 5′-

hexamethylbenzophenoneoxime], which crystallises in short, almost white needles, m. p. 186—187°, and remains unchanged when boiled with acetic anhydride and sodium acetate.

With bromine in glacial acetic acid solution it yields a *tribromo*-derivative, crystallising in lustrous, white needles, m. p. 207—208°. Although this tribromo-derivative probably contains one of the bromine atoms directly united with the central carbon atom it remains unchanged even on prolonged heating with alcoholic potassium hydroxide.

aaa-Tribromo-2 : 4 : 5 : 2′ : 4′ : 5′-*hexamethyl-ββ-diphenylethane*, $CBr_3 \cdot CH(C_6H_2Me_3)_2$, prepared by condensing ψ-cumene and bromal hydrate with sulphuric acid in glacial acetic acid solution, crystallises in long, lustrous, white needles, m. p. 141—142°, and on treatment with bromine yields a *pentabromo*-derivative, $C_{20}H_{21}Br_5$, which forms lustrous leaflets or small, octahedral crystals, m. p. 188—191°. When heated with alcoholic potassium hydroxide it is converted into *aa*-dibromo-2 : 4 : 5 : 2′ : 4′ : 5′-*hexamethyl-ββ-diphenylethylene*, $CBr_2{:}C(C_6H_2Me_3)_2$, short, stout prisms, m. p. 100—102°.

as-2 : 4 : 5 : 2′ : 4′ : 5′-Hexamethyldiphenylethane, $CHMe(C_6H_2Me_3)_2$, prepared by the successive addition of paracetaldehyde and ψ-cumene to sulphuric acid at −5°, crystallises in lustrous, short, white prisms, m. p. 126—127°; Elbs (A., 1893, i, 271) gives m. p. 117—120°.

F. B.

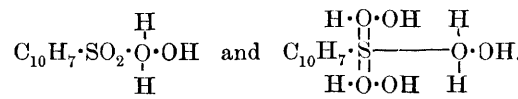
The Naphthalenemonosulphonic Acids. Otto N. Witt (*Ber.*, 1915, **48**, 743—772).—A review and extension of our knowledge of the chemistry of the naphthalenesulphonic acids, dealing especially with the preparation of β-naphthalenesulphonic acid.

The sulphonation of naphthalene under no conditions yields the α- or β-isomeride to the exclusion of the other, and the chemical change is still further complicated by certain by-reactions, giving rise to a mixture of the isomeric dinaphthylsulphones with certain oxidation products and tarry condensation products. As these impurities are soluble in the aqueous solution of the sulphonic acids the purification of the latter is rendered much more difficult. For the separation of the acids from the accompanying foreign substances and from one another in the raw product obtained by sulphonation at lower temperatures, conversion into the lead, barium or calcium salts does not entirely obviate the difficulties. With the reaction product obtained at higher temperatures in which the β-acid predominates, treatment with sodium chloride provides a fairly satisfactory means of separating the β-acid as its sodium salt if the quantity of sulphuric acid originally taken was kept below a certain limit. A method is now described by which it is possible conveniently to obtain the β-acid in considerable quantities in a state of purity.

By maintaining 220 grams of pure naphthalene at 160° whilst 400 grams of concentrated sulphuric acid (93·7%) are gradually introduced with continuous stirring, sulphonation can be effected with an almost entire exclusion of side reactions, the only product other than the sulphonic acids being the dinaphthylsulphones, of which the

total quantity may reach 1%. The addition of acid is complete in fifteen minutes, after which the heating may be extended for another five minutes. The reaction product is poured into 2 litres of cold water, when after twenty-four hours the sulphones will have almost completely separated in a filterable condition; the remainder can be extracted by shaking with a little benzene. For the separation of the β-naphthalenesulphonic acid from the solution, use is made of the discovery that this acid is readily "salted out" from solution by other acids, such as hydrochloric and phosphoric acids; thus the acid is almost insoluble in cold 10% hydrochloric acid solution, and separates out almost quantitatively therefrom at 10° as a trihydrate. α-Naphthalenesulphonic acid and the naphthalenedisulphonic acids exercise the same "salting out" effect, so that to cause the β-isomeride to separate it is merely necessary to evaporate the solution by boiling until its temperature attains 115°, when under the influence of the dissolved α-isomeride the β-acid separates to a crystalline mass on cooling. It is also obvious that a similar result can be produced by suitably diluting the crude reaction product, but in this case the sulphones will contaminate the product. It is found that the crude sulphonation mixture contains the α- and β-isomerides in the proportion of 15 parts to 85, at least 80 parts of the latter being deposited as trihydrate under the described conditions; the mother liquors contain the α- and β-acids in the approximate ratio 10 : 1. The β-acid is purified by dissolving 600 grams in 300 c.c. of water at 70°, and allowing to cool after the addition of 100 c.c. of hydrochloric acid (D 1·19).

When obtained in this way the product is a beautifully crystalline β-naphthalenesulphonic acid *trihydrate*, $C_{10}H_7\cdot SO_2\cdot OH,3H_2O$, m. p. 83°; this undergoes dehydration when kept in a vacuum over sulphuric acid or calcium chloride, yielding the already known monohydrate, m. p. 124°, which gradually combines with atmospheric moisture regenerating the trihydrate. Contrary to the statements of earlier investigators, the acid is not deliquescent. The last molecule of water is very tenaciously retained by β-naphthalenesulphonic acid, but the acid was obtained anhydrous, probably for the first time, by exposing to a current of dry air at the temperature of boiling toluene. The anhydrous acid, m. p. 90·5—91°, is enormously hygroscopic, but not deliquescent; it is readily soluble in solvents such as benzene or phenol in which the trihydrate is insoluble, but the crystals obtained from such solutions always consist of a more or less re-hydrated substance. At the b. p. of aniline the anhydrous acid yields yet another molecule of water with formation of a vitreous mass which dissolves in water to a milky liquid; this *substance* is probably of similar nature to the resinous by-products formed during the sulphonation of naphthalene. Attention is drawn to the ease with which the hydrated derivatives of β-naphthalenesulphonic acid may be represented by the structures



and

Relatively little is known of the salts of β-naphthalenesulphonic acid, and descriptions of the following are given; the salts are generally sparingly soluble and readily crystallise, consisting almost invariably of tetragonal tablets with truncated corners; ammonium salt, crystals of the monoclinic, prismatic system; potassium salt, with $\frac{1}{2}H_2O$; sodium salt; silver salt; barium salt; calcium salt; lead salt, with $1H_2O$; zinc salt, with $6H_2O$; cobalt salt, flesh-red tetragonal or hexagonal leaflets with $6H_2O$; nickel salt, green crystals with $6H_2O$, yellow when anhydrous; cadmium salt with $6H_2O$, undergoes complete dehydration at 80°; copper salt, blue crystals with $6H_2O$, loses $4H_2O$ at 75—80°, giving a colourless solid, and at 125° becomes anhydrous and yellow. D. F. T.

Triarylmethyls. XIII. The Metaquinonoid Question. W. Schlenk and Max Brauns (*Ber.*, 1915, **48**, 661—669).—Stark who, with various colleagues, has investigated a hydrocarbon which is formed when the halogen of tetraphenyl-*m*-xylylene dichloride is removed by metals (A., 1913, i, 361, 849, 1165; 1914, i, 267) stated in his last paper that the preparation of the so-called metaquinonoid "tetraphenyl-*m*-xylylene" could not be guaranteed, and invited the co-operation of other workers in this field. The authors have now found that the difficulties are intimately connected with the purity of the starting materials.

In order to be quite sure that the *iso*phthalic acid was free from terephthalic acid, which was found to be impossible if *m*-xylene is chosen as the source, it was prepared by oxidising *m*-ditolyl, which was obtained from *o*-toluidine by a modification of Winston's method (A., 1904, i, 274). The methyl *iso*phthalate, m. p. 66—67°, was converted by the agency of magnesium phenyl bromide (a process which gives constant results is described) into tetraphenyl-*m*-xylylene glycol and this into the dichloride, m. p. 140·5°.

When prepared in this way, the dichloride behaved quite differently from the account given by Stark. When a benzene solution was shaken with "molecular" silver in an atmosphere of pure carbon dioxide, it did indeed become deep yellow, but this colour immediately disappeared on admitting oxygen. The colour gradually re-appeared, but paled again on shaking with air and this process could be repeated a few times until the solution remained permanently colourless. This was to be explained by the formation of a peroxide from a triarylmethyl radicle, for the yellow solution had the characteristic spectrum of such compounds, namely a very dark band from λ 513—517 and then complete absorption from λ 493 to the end of the visible spectrum. This stage represented the removal of one atom of chlorine, for when the final solution was added to molten phenol, it developed the characteristic deep reddish-brown colour given by triarylmethyl haloids, but not by the free triarylmethyls. The elimination of the remaining chlorine atom took place when the benzene solution was boiled with copper "bronze" in an atmosphere of carbon dioxide. The solution became deep violet, and showed a dark band from λ 576—636, but, on shaking with air, the colour disappeared instantaneously, indicating the presence of the bistriaryl-

methyl radicle. The violet solution was evaporated to a small bulk in the absence of air, and then colourless crystals of a very sparingly soluble *hydrocarbon*, $(C_{32}H_{24})_x$, probably a polymeride of the free radicle, were deposited.

Stark expressly stated that his yellow solution was completely stable towards oxygen, but this may be due to the fact that his materials were not free from para-isomerides and therefore the final solution contained tetraphenylquinodimethane, traces of which would give all the characteristics which were assigned to the metaquinonoid hydrocarbon.

The formation of the two radicles, thus : $CPh_2Cl{\cdot}C_6H_4{\cdot}CPh_2Cl \longrightarrow CPh_2Cl{\cdot}C_6H_4{\cdot}CPh_2 \longrightarrow CPh_2{\cdot}C_6H_4{\cdot}CPh_2$, is another indication that metaquinonoid compounds do not exist. J. C. W.

Triarylmethyls. XV. Some Bistriarylmethyls. W. Schlenk and Max Brauns (*Ber.*, 1915, **48**, 716—728).—I. *Bistriarylmethyls of the Diphenyl Series.*—Schmidlin (A., 1913, i, 32) stated that Schlenk's tridiphenylylmethyl contained a blue isomeride, and the latter author replied (*ibid.*, 610) by pointing out that the supposed β-compound was in reality 4 : 4′-dipnenylenebisbidiphenylylmethyl,

$$(C_6H_4Ph)_2C{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}C(C_6H_4Ph)_2.$$

As it was promised, this hydrocarbon has now been synthesised. The nearly related compound 4 : 4′-diphenylenebisdiphenylmethyl,

$$CPh_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CPh_2$$

(Tschitschibabin, A., 1907, i, 503) has also been made for comparison, by a simpler method. Attempts have also been made to prepare derivatives analogous to the latter in the ortho-series. It was found, however, that the necessary 2 : 2′-diphenylenebisdiphenylcarbinol too readily formed a stable anhydride. On the other hand, a meta-derivative could be obtained, but this was found to be very different from the above para-compound. The solutions were only orange in colour and the solid was colourless. In this state, it is regarded as a symmetrical dimeride containing a 12-carbon ring.

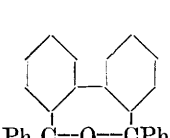
p-Iododiphenyl was converted into the Grignard compound, and this was warmed with finely powdered methyl diphenyl-4 : 4′-dicarboxylate. The product was decomposed by dilute sulphuric acid and 4 : 4′-*diphenylenebisbidiphenylylcarbinol*, $OH{\cdot}C(C_6H_4Ph)_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}C(C_6H_4Ph){\cdot}OH$, was finally obtained in colourless, microscopic needles, m. p. above 260°, which gave a deep violet solution in concentrated sulphuric acid with a band at λ 610—480. The *dichloride*, $C_{62}H_{44}Cl_2$, was prepared in xylene solution and crystallised with 1 mol. xylene in colourless needles, m. p 271°. A benzene solution of this was boiled with copper powder in an atmosphere of carbon dioxide, and 4 : 4′-*diphenylenebisbidiphenylylmethyl* was obtained in needles with brilliant green reflection. The solutions had beautiful dark blue colours, which disappeared immediately on shaking with air, but no peroxide could be isolated.

The chief improvement in the preparation of 4 : 4′-diphenylenebisdiphenylmethyl consisted in preparing the necessary 4 : 4′-diphenylene-

bisdiphenylcarbinol (*loc. cit.*) by the action of magnesium phenyl bromide on 4 : 4′-*dibenzoyldiphenyl*, $C_6H_4Bz{\cdot}C_6H_4Bz$. This was prepared by warming together equal weights of diphenyl, aluminium chloride and benzoyl chloride. It crystallised from nitrobenzene in silvery leaflets, m. p. 216°.

Methyl diphenylene-3 : 3′-dicarboxylate (Ullmann, A., 1904, i, 725) was converted by the agency of magnesium phenyl bromide into 3 : 3′-*diphenylenebisdiphenylcarbinol*, $OH{\cdot}CPh_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CPh_2{\cdot}OH$, tablets, m. p. 183—184°, this into the *dichloride*, $C_{38}H_{28}Cl_2$, lancets, m. p. 175—176°, and the latter was dissolved in benzene and shaken with mercury in a sealed tube filled with carbon dioxide. 3 : 3′-*Diphenylenebisdiphenylmethyl*, $(C_{38}H_{28})_n$, was thus obtained in colourless, short needles. It gave an orange solution with bands at λ 512—520 and λ 481—493 in benzene, which became pale on shaking with air, regained the colour after a time, lost it again on treatment with more air, and so on, until after repeating the performance about ten times, the colour was permanently pale yellow. This showed that the free triarylmethyl was considerably associated even in solution, which was also proved cryoscopically.

Methyl diphenate and magnesium phenyl bromide yielded a carbinol which lost water when an attempt was made to convert it into the chloride. The product, *anhydro*-2 : 2′-*diphenylenebisdiphenylcarbinol* (annexed formula), formed colourless crystals, m. p. 291—293°.



II. *Attempts to prepare tetraphenyl-o-xylylene.*—The difference in structure between Thiele's tetraphenyl-*p*-xylylene [tetraphenylquinodimethane] and tetraphenyl-*m*-xylylene, a bistriarylmethyl (compare this vol., i, 517), has led the authors to attempt the preparation of the *ortho*-analogue, but they were not successful, for the necessary carbinol too readily formed an inner anhydride.

Magnesium phenyl bromide and phthalophenone gave *tetraphenyl-o-xylylene glycol*, $OH{\cdot}CPh_2{\cdot}C_6H_4{\cdot}CPh_2{\cdot}OH$, in prismatic crystals, m. p. 198°, and this changed into *tetraphenylphthalane*, $C_6H_4<\begin{matrix}CPh_2\\CPh_2\end{matrix}>O$, needles, m. p. 174—175°, when treated with any dehydrating agent.

J. C. W.

αδ-Bisdiphenylene-Δ$^{\alpha\gamma}$-butadiene. Wilhelm Wislicenus [with Funke, Liebold and Fehrle] (*Ber.*, 1915, **48**, 617—624).—The author has often observed that when condensations with fluorene are carried out in the presence of alkali ethoxides, a small amount of an orange to deep red hydrocarbon is formed, which, on recrystallisation, yields the same yellowish-red hydrocarbon as was originally obtained by the alternate action of sodium ethoxide and ethyl formate on an alcoholic solution of fluorene (Wislicenus and Densch, A., 1902, i, 291). It is now shown that the compound is formed by the action of alcoholic ethoxides alone on fluorene, but that good yields are only possible in the presence of air, which accounts for the fact that Mayer (A., 1913, i, 1171) could not obtain it at all. Moreover, the substance is recognised as αδ-bisdiphenylene-Δ$^{\alpha\gamma}$-butadiene, for it can be reduced to the

definitely characterised $\alpha\delta$-bisdiphenylenebutane (A., 1913, i, 1188). It is also suggested that it was this same hydrocarbon which Pummerer and Dorfmüller (A., 1913, i, 963) called "dehydroethylidenebisfluorene," Mayer (*loc. cit.*) obtained as a "red hydrocarbon," and Stollé (A., 1913, i, 1171) designated "dehydrobenzylidenebisfluorene."

Fluorene (1 mol.) was dissolved in ether and mixed with a solution of potassium ($1\frac{1}{2}$ mols.) in alcohol, when the liquid soon developed a dark red colour which paled somewhat when submitted to a current of air or oxygen. The mixture was treated with oxygen for a short time every day for about five weeks, when a 50% yield of the coloured hydrocarbon was deposited. The crude material was extracted with boiling xylene, which removed a little of a dark red compound, and then *$\alpha\delta$-bisdiphenylene-$\Delta^{\alpha\gamma}$-butadiene*, $\begin{matrix}C_6H_4\\ \vert\\ C_6H_4\end{matrix}\!>\!C{:}CH{\cdot}CH{:}C\!<\!\begin{matrix}C_6H_4\\ \vert\\ C_6H_4\end{matrix}$, was obtained in prisms of the colour of potassium dichromate, m. p. 372—374° (thermometer quite immersed). It yielded fluorenone on oxidation, fluorene when distilled with zinc dust, and formed a colourless *tetrachloride*, m. p. 215—219°, and a characteristic *dipicrate*, stellar aggregates of reddish-brown needles, m. p. about 260° (decomp.), which is useful for purposes of purification. It was reduced by zinc and glacial acetic acid to *$\alpha\delta$-bisdiphenylene-Δ^{β}-butene*, $C_{28}H_{20}$, glistening, yellow needles, m. p. 267—268°, and by phosphorus and hydriodic acid to $\alpha\delta$-bisdiphenylenebutane, colourless prisms, m. p. 224—225°. The latter was also obtained from the butene by reduction with sodium amalgam. J. C. W.

Bromination of Aromatic Amines. Walter Fuchs (*Monatsh.*, 1915, **36**, 113—141).—Acetic acid appears to be the most favourable solvent for the bromination of aromatic amines, and an examination has been made of the behaviour of many amines towards bromine in this medium. The usual method of procedure was to introduce the calculated quantity of a solution of 50 grams of bromine in 200 c.c. of the solvent into the cooled solution of the base. If so desired, the resulting hydrogen bromide could be removed by the addition of sodium or ammonium acetate, and it was also observed that in some cases the addition of a little water towards the end of the reaction was advantageous. Finally, the brominated base was caused to separate by the addition of water, and the product was generally satisfactory both from the point of view of quantity and purity. Meta-substituted anilines and aniline itself tend to give rise to dibromo-derivatives, whereas ortho- and para-substituted anilines generally give dibromo-derivatives, sometimes with replacement of another acidic substituent, such as $-SO_2{\cdot}OH$ or $-CO_2H$, but the number of bromine atoms actually introduced is dependent on the experimental conditions, more particularly the concentration of the bromine solution. With regard to the position taken by the substituent bromine atom, it is noted that the amino-group is of greater directive influence than any other group which may be present. If an acidic group is present in the ortho-position to the amino-radicle, the bromine atom enters almost quantitatively at the para-position. Witt's methods for the preparation and

reduction of diazo-compounds (A., 1909, i, 855) proved of great value in determining the structure of the products.

In the course of the investigation it was found that under the described conditions, *p*-toluidine gave rise to 2 : 6-dibromo-*p*-toluidine; *p*-aminoacetanilide to 3 : 5-*dibromo*-4-*aminoacetanilide*, colourless, silky needles, m. p. 239° (decomp.); *p*-aminoacetophenone to 3 : 5-*dibromo*-4-*aminophenyl methyl ketone*, colourless, prismatic crystals, m. p. 180° (which gives a *phenylhydrazone*, golden-yellow needles, m. p. indistinct at 146°, and is convertible by diazotisation into 3 : 5-dibromoacetophenone, colourless needles, m. p. 66°); sulphanilic acid to *s*-tribromoaniline and 2 : 6-dibromoaniline-*p*-sulphonic acid; sulphanilamide to 2 : 6-dibromoaniline-*p*-sulphonamide, leaflets, m. p. 237°; *p*-phenetidine to 3 : 5-*dibromo*-4-*aminophenyl ethyl ether*, silky needles, m. p. 79°; *o*-toluidine to 4 : 6-dibromo-*o*-toluidine; *o*-aminobenzaldehyde to 3 : 5-dibromo-2-aminobenzaldehyde; *o*-aminoacetophenone to 3 : 5-*dibromo*-2-*aminophenyl methyl ketone*, golden-yellow rods, m. p. 130°; *o*-anisidine to 3 : 5-*dibromo*-2-*aminophenyl methyl ether*, a yellow oil (*hydrochloride*, needles; *acetyl* derivative, prismatic crystals, m. p. 145°); *o*-aminophenol to 3 : 5-dibromo-2-aminophenol (which, however, was not obtainable crystalline or colourless); aniline to *s*-tribromoaniline or *p*-bromoaniline, according to the conditions of the experiment; *m*-toluidine to 2 : 4 : 6-tribromo-*m*-toluidine; *m*-nitroaniline to 2 : 4 : 6-tribromo-, 4 : 6-dibromo- or 4-bromo-3-nitroaniline, according to the conditions; *m*-phenylenediamine to a brown substitution *product*, which could not be purified; *m*-aminobenzaldehyde to 2 : 4 : 6-tribromo-3-aminobenzaldehyde; *m*-aminoacetophenone to 2 : 4 : 6-*tribromo*-3-*aminophenyl methyl ketone*, prisms, m. p. 121° (it gave a *phenylhydrazone*, needles, m. p. 120°, and by the diazo-reaction was convertible into 2 : 4 : 6-tribromoacetophenone, needles, m. p. 93·5°, which on oxidation with alkaline permanganate solution gave 2 : 4 : 6-*tribromophenylglyoxylic acid*, needles, m. p. 174° (acid permanganate solution oxidised this to *s*-tribromobenzoic acid); *o*-nitroaniline to 4-bromo-2-nitroaniline, and anthranilic acid to 5-bromoanthranilic acid. D. F. T.

The Nature of Subsidiary Valencies. X. Limits of Stability of Complex Anions. II. FRITZ EPHRAIM and ERNST HOCHULI (*Ber.*, 1915, **48**, 629—637. Compare A., 1914, i, 827; and this vol., ii, 166).—The dissociation pressures of the hydrochlorides of the following bases have been measured at various temperatures; *p*-iododimethylaniline, dimethylaniline, benzylmethylaniline, diamylaniline, pyridine, piperidine, quinaldine, quinine, strychnine, azobenzene, dimethylpyrone, *p*-benzoquinone and acetanilide. Methylallylaniline, dipropylaniline, dimethyl-*o*-4-xylidine and α-picoline combined readily with at least two molecules of hydrogen chloride, but the products could not be crystallised. A *bromo*-3-*nitrodimethylaniline*, $C_8H_9O_2N_2Br$, obtained in silky, orange needles, m. p. 94°, by brominating *m*-nitrodimethylaniline, formed a *monohydrochloride* which had no measurable tension at 130°.

The tensions of the dihydrobromides of diethylaniline, pyridine and quinoline were also measured, but dimethylaniline, dimethyl-*o*-toluidine and benzylmethylaniline only gave liquid salts. The dihydriodides of

quinoline, diethylaniline and benzylmethylaniline were also examined. A table is given in which the temperatures at which these salts and those described in the seventh paper (A., 1914, i, 827) develop 350 mm. pressure are recorded. It is evident that the acid chlorides are generally more stable than the corresponding bromides, and much more so than the iodides. J. C. W.

Preparation of Salts of Phenylcarbamic Acid. EDUARD KOPETSCHNI (*Ber.*, 1914, **47**, 2987—2990).—Houben and others found that the magnesium iodide salts of phenylcarbamic acids derived from secondary bases undergo rearrangement into derivatives of *p*-aminobenzoic acid when heated, whereas those derived from primary bases merely suffer decomposition (A., 1909, i, 921 ; 1910, i, 34, 110). The author has now tried the effect of heat on simple, anhydrous, alkali salts of phenylcarbamic acid.

Small pieces of sodium were mixed with fifty times as much aniline in a bomb, which was then filled with carbon dioxide under 45 atmos. and heated in an electric oven at 220—240°. Impure *sodium phenylcarbamate* separated on cooling as a voluminous powder. *Potassium phenylcarbamate*, $NHPh\cdot CO_2K$, was made by passing a brisk current of dry carbon dioxide through a large excess of aniline at the ordinary temperature and introducing small pieces of the metal from time to time. It is a white powder. The salts are very soluble in water but the solutions soon deposit aniline. They suffer decomposition into aniline (with traces of carbanilide and phenylcarbylamine) and sodium carbonate (with a trace of an aminobenzoic acid in the case of the potassium salt) on heating at 250—260° in an indifferent atmosphere, and react with ethyl iodide to give ethylanilines and not the expected phenylurethane. J. C. W.

Dehydration and Esterification of *cyclo*Hexanol and of 4-Methyl*cyclo*hexan-1-ol by Oxalic Acid. A. JUÉRY (*Bull. Soc. chim.*, 1915, [iv], **17**, 167—175. Compare Zelinski and Zelikoff, A., 1902, i, 2).—The action of oxalic acid on *cyclo*hexanol or its homologue when they are heated together varies according to the proportions of acid and alcohol used.

When *cyclo*hexanol (1 mol.) is heated with oxalic acid ($\frac{1}{4}$ mol.), about 80% of the alcohol remains unaltered, the remainder being converted into cyclo*hexyl oxalate*, small, white crystals, m. p. 45°, b. p. 190—191°/13 mm., together with a trace of *cyclo*hexene. If the molecular proportions of alcohol and acid are 1 : 1 or 1 : 3, the main product is *cyclo*hexene, the rest of the alcohol being recovered unchanged.

If 4-methyl*cyclo*hexan-1-ol (1 mol.) is heated with oxalic acid ($\frac{1}{2}$ mol.), 30% of the alcohol is recovered unchanged, the remainder being esterified. The product contains a solid and a liquid 4-*methyl*cyclo*hexyl oxalate*, which are apparently *cis-trans*-isomerides. The solid has m. p. 98°, b. p. 192—193°/27 mm. The liquid has b. p. 198—199°/16 mm., D^0 1·044, and does not solidify even when cooled in methyl chloride. The two isomerides yield the same original alcohol on saponification, and in their preparation the proportion of solid to liquid

obtained is invariably 1 : 2. If, in this preparation, equimolecular proportions of alcohol and acid are taken, 50% of the alcohol is recovered unchanged and the remainder is converted into equal parts of 4-methyl*cyclo*hexene and the oxalate mentioned above. If the proportions of alcohol and acid used are 1 : 3, about 50% of the alcohol is dehydrated and the remainder is recovered unchanged. W. G.

Solubility of Salts of Nitrophenols in Mixtures of Alcohol and Water. V. M. FISCHER (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1250—1270).—According to Goldschmidt (A., 1895, ii, 382), the solubility of salts crystallising with water should be increased by addition of alcohol, carbamide, glycerol or, in general, any non-electrolyte, as the latter raises the transition point of the higher hydrate into the lower or into the anhydrous salt; this conclusion assumes, however, that the solubility of the anhydrous salt is changed either not at all or but little by addition of the non-electrolyte. From the results of their experiments, Loewenherz (A., 1896, ii, 149) and Hudson (A., 1909, ii, 131) assert that Goldschmidt's rule cannot be generalised, since only in rare cases does the solubility of an anhydrous salt remain unchanged on addition of a non-electrolyte. Thus, the solubility of decahydrated sodium sulphate is markedly lowered by carbamide, or else the lowering of the solubility of the anhydrous salt is greater than the increase in solubility of the hydrate. Further, the solubilities of barium, calcium, and strontium nitrates in water are depressed by addition of alcohol (compare D'Ans and Siegler, A., 1913, ii, 214).

The author finds that the solubility of sodium picrate ($+H_2O$) in mixtures of alcohol and water at 25° exhibits two minima, at 25 and 95—99 vol. % of alcohol respectively and a maximum at 50 vol. %; in absolute alcohol the solubility is greater than in water. Similar solubility isotherms, with two minima and one maximum, are shown by barium ($+5H_2O$) and potassium picrates, tetra- and di-hydrated sodium *p*-nitrophenoxides, sodium 3 : 4-dinitrophenoxide ($+H_2O$), sodium 4-chloro-3-nitrophenoxide ($+H_2O$), and barium dinitrosalicylate. In mixtures of acetone and water, a maximum of solubility is shown by potassium picrate and sodium 3 : 4-dinitrophenoxide, which thus resemble potassium permanganate and boric and succinic acids (compare Herz and Knoch, A., 1904, ii, 709). In mixtures of methyl alcohol and water, the sodium dinitrophenoxide exhibits a minimum solubility at 95—96 vol. % of the alcohol, and in the absolute alcohol is more soluble than in water, as was found by Bruyn (A., 1893, i, 244) for hydrated salts in absolute methyl and ethyl alcohols. The solubility of potassium picrate is lowered at first slowly and afterwards more rapidly by addition of methyl alcohol, the curve changing direction at 60 vol. % of the alcohol.

The maximal and minimal solubilities of the salts of the nitrophenols in mixtures of ethyl alcohol and water are displaced in one or the other direction according to the nature of the salt and to the temperature, so that the influence of the hydration of the alcohol as the cause of the phenomenon is excluded. Further, the degree of dissociation of these salts in mixtures of alcohol and water exhibits no

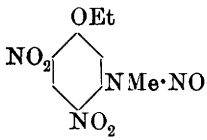
abnormality (compare Cohen, A., 1898, ii, 154), and the viscosity of the solutions shows no discontinuity, so that the variation in the solubility is not due to the presence of hydrates.

The author regards the anomalous solubility curves of salts of the nitrophenols in aqueous ethyl alcohol as due to displacement of the equilibrium, $NO_2 \cdot C_6H_4 \cdot ONa \rightleftarrows O:C_6H_4:N(ONa):O$. This explanation is supported by the observation that the coefficient of extinction of these solutions does not change linearly with the concentration of the alcohol, and also by the results of Scharvin (A., 1910, ii, 396), Waliaschko (A., 1910, ii, 1015), and Bortini (A., 1914, ii, 400).

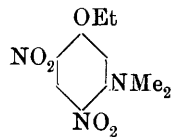
The numerical results of the solubility measurements are given in detail. T. H. P.

Nitration of Dimethyl-*m*-phenetidine. FRÉDÉRIC REVERDIN (*Bull. Soc. chim.*, 1915, [iv], **17**, 190—196. Compare Reverdin and de Luc, A., 1914, i, 831).—A comparison of the action of nitric acid under different conditions on dimethyl-*m*-phenetidine and dimethyl-*m*-anisidine. The dimethyl-*m*-phenetidine used was prepared by the action of methyl sulphate on *m*-phenetidine, the product of the reaction being treated with aqueous sodium hydroxide.

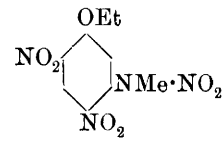
When nitric acid (D 1·4) is slowly added to a solution of dimethyl-*m*-phenetidine cooled in a freezing mixture no action occurs, but if the temperature is then slowly raised to 70° nitration occurs, and, on pouring the mixture into water, a yellow precipitate separates. On crystallisation from alcohol and finally from benzene, this yields pale yellow needles of 4:6-*dinitro*-3-*nitrosomethylaminophenetole* (I.), m. p. 113—114°.



(I.)



(II.)



(III.)

If the temperature is only raised to 25° the nitration takes longer, and the product is a mixture of this nitrosoamine and 4 : 6-*dinitro*-3-*dimethylaminophenetole* (II.), yellow needles, m. p. 172°. These two compounds are separable owing to their differing solubilities in alcohol. If, during the nitration, the temperature only rises to 12°, the compound, m. p. 172°, is the only product.

By the action of nitric acid (D 1·25) on the nitrosoamine dissolved in acetic anhydride, or on the original base in the same solvent at 20°, 4 : 6-*dinitro*-3-*methylnitroaminophenetole* (III.), m. p. 137—138°, is obtained. If the nitrosoamine, m. p. 113—114°, is boiled for one hour with moderately concentrated hydrochloric acid it is converted into 4 : 6-*dinitro*-3-*methylaminophenetole*, yellow needles, m. p. 210°. This compound is also obtained by boiling the nitroamine, m. p. 137—138°, with phenol.

The position of the nitro-groups in these compounds is shown by the fact that when the nitroamine is boiled with alcoholic potassium hydroxide for one hour, and the resulting potassium salt decomposed

by hydrochloric acid, 4 : 6-dinitro-3-methylaminophenol, m. p. 182° (compare Reverdin and de Luc, *loc. cit.*), is obtained.

A comparison of the behaviours of dimethyl-*m*-phenetidine and dimethyl-*m*-anisidine on nitration shows that the only difference is that in the case of dimethyl-*m*-phenetidine, the temperatures at which the reactions commence are higher than with the other base, the products of the reactions being similar in each case.

The author has now succeeded in preparing 4 : 6-*dinitro*-3-*methyl-nitrosoaminoanisole* in yellow needles, m. p. 115°, by the action of nitric acid, under the conditions set out above, substituting dimethyl-*m*-anisidine for dimethyl-*m*-phenetidine, and allowing the temperature to rise to 45° before pouring the product into water. W. G.

Behaviour of Phenols with Unsaturated Side-Chains towards Ozone. Otto N. Witt (*Ber.*, 1915, **48**, 231—233, 698—699; C. Harries, *ibid.*, 410).—Polemical. J. C. W.

Action of Organo-magnesium Compounds on Methyl 1-Hydroxy-β-naphthoate. Franz Preissecker (*Monatsh.*, 1914, **35**, 889—908).—Magnesium ethyl iodide reacts with methyl 1-hydroxy-β-naphthoate, yielding β-1-*hydroxy*-2-*naphthylpropylene*,

$$OH\cdot C_{10}H_6\cdot CMe{:}CH_2,$$

which crystallises in colourless prisms, m. p. 121—122°, gives a red coloration with ferric chloride, and on treatment with bromine in carbon tetrachloride solution is converted into α-*bromo*-β-1-*hydroxy*-2-*naphthylpropylene*, $OH\cdot C_{10}H_6\cdot CMe{:}CHBr$, m. p. 191—193° (decomp. 198°).

γ-1-*Hydroxy*-2-*naphthylpentan*-γ-*ol*, $OH\cdot C_{10}H_6\cdot CEt_2\cdot OH$, prepared from the methyl ester and magnesium ethyl iodide, has m. p. 80—81°.

The action of magnesium phenyl bromide results in the formation of diphenyl-1-hydroxy-β-naphthylcarbinol, $OH\cdot C_{10}H_6\cdot CPh_2\cdot OH$, large, prismatic crystals, m. p. 119—121° with previous reddening at 110°, and β-naphthafuchsone (2-diphenylmethylene-1-naphthaquinone),

$$C_{10}H_6O{:}CPh_2,$$

deep red prisms of rhombic section, m. p. 138—139° (compare Kauffmann and Egner, A., 1914, i, 139).

The last-named substance reacts with hydroxylamine in alcoholic solution, yielding 2-*hydroxylaminodiphenylmethyl*-1-*naphthaquinoneoxime*, $C_6H_4\langle{}^{C(N\cdot OH)\cdot CH\cdot CPh_2\cdot NH\cdot OH}_{CH=\!=\!=CH}$, lustrous, silky, white needles, m. p. 142°, and is reduced by zinc dust and glacial acetic acid to *diphenyl*-1-*acetoxy*-β-*naphthylmethane*, $OAc\cdot C_{10}H_6\cdot CHPh_2$, which forms pale yellow leaflets, m. p. 92—93°, and on hydrolysis with alcoholic hydrogen chloride is converted into the original quinone.

2-αα-*Dinaphthylmethylene*-1-*naphthaquinone*,

$$C_6H_4\langle{}^{CO\cdot C{:}C(C_{10}H_7)_2}_{CH{:}C},$$

prepared from methyl 1-hydroxy-β-naphthoate and magnesium α-naphthyl bromide, crystallises in dark red, microscopic prisms, m. p. 173—175°, gives an indigo-blue coloration with sulphuric acid and is

reduced by zinc dust and acetic acid to *αα-dinaphthyl-1-acetoxy-β-naphthylmethane*, $OAc\cdot C_{10}H_6\cdot CH(C_{10}H_7)_2$, pale yellow, leafy crystals, m. p. 103—105° (decomp.). F. B.

Compounds of Catechol and Phenol with Alkaline or Alkaline Earth Salts of Various Acids. R. F. Weinland and Wilhelm Denzel (*Ber.*, 1914, **47**, 2990—2994).—Other examples of the behaviour of phenolic substances as alternatives to the water molecules in aquo-salts are described (compare A., 1914, i, 525, 953).

Solutions of potassium benzenesulphonate and catechol (1—4 mols.) deposit the *compound*, $C_6H_5\cdot SO_3K,C_6H_4(OH)_2$, in thin, hexagonal, glistening leaflets. Alcoholic solutions of anhydrous calcium chloride and catechol (3—4 mols.) give the *compound*, $\left[Ca\begin{matrix}(C_6H_6O_2)_4\\(C_2H_5\cdot OH)_2\end{matrix}\right]Cl_2$, in well-developed, colourless crystals. A solution of sodium acetate (1 mol.), catechol (2 mols.) and acetic acid (1 mol.) deposits the *compound*, $\left[Na\begin{matrix}(C_6H_6O_2)_2\\Me\cdot CO_2H\end{matrix}\right]OAc$, in long, stout, hexagonal plates. The *compound*, $2C_6H_5\cdot OH,Me\cdot CO_2K$, crystallises in large tablets from alcoholic solutions of potassium acetate and phenol (1—5 mols.)

J. C. W.

Dihydric Alcohols obtained by the Reduction of Substituted Dihydroresorcins. Arthur William Crossley and Nora Renouf (T., 1915, **107**, 602—610).—In an earlier paper (T., 1908, **93**, 629), a method has been described for obtaining substituted *cyclo*hexadienes from 1 : 3-dibromo-derivatives of the saturated *cyclo*hexanes. As it was considered probable that these substances could be more readily obtained from dihydric alcohols, a study has been made of the dihydric alcohols formed by the reduction of substituted dihydroresorcins with sodium and alcohol (compare Zelinski and Uspenski, A., 1913, i, 607). The dihydric alcohols are crystalline compounds, are neutral to litmus, readily yield dibenzoyl derivatives, and do not absorb bromine in chloroform solution. In many respects they resemble glycols as they have a sweet taste and are easily soluble in water but not in ether.

On reducing dimethyldihydroresorcin, 1 : 1-dimethyl*cyclo*hexane-3 : 5-diol, $CMe_2\begin{matrix}<CH_2\cdot CH(OH)\\<CH_2\cdot CH(OH)\end{matrix}>CH_2$, m. p. 147°, is obtained in a yield of 66—68% of the theoretical together with 7—10% of 1 : 1-dimethyl*cyclo*hexan-3-ol; the *o-nitrobenzoyl* derivative of the latter compound has m. p. 62°. The *dibenzoyl* derivative of 1 : 1-dimethyl-*cyclo*hexane-3 : 5-diol, m. p. 135—136°, forms transparent, flattened needles.

Methyldihydroresorcin on reduction furnishes 1-methyl*cyclo*hexane-3 : 5-diol together with 1-methyl*cyclo*hexan-3-ol, the *o-nitrobenzoyl* derivative of which has m. p. 54°. 1-*Methyl*cyclo*hexane*-3 : 5-*diol*, m. p. 75°, crystallises in radiating clusters of glistening needles; its *dibenzoyl* derivative has m. p. 81°. From the mother liquors a small quantity of a *substance*, m. p. 143·5°, was isolated which probably consisted of an isomeric form of the diol.

By the reduction of trimethyldihydroresorcin, 1 : 1 : 2-trimethyl*cyclo*-

hexan-3-ol and 1 : 1 : 2-*trimethyl*cyclo*hexane*-3 : 5-*diol*, m. p. 150°, are produced. The latter compound crystallises in nacreous, flattened needles, and furnishes a *dibenzoyl* derivative, m. p. 97°.

*iso*Propyldihydroresorcin similarly yields 1-*iso*propyl*cyclo*hexan-3-ol, and 1-iso*propyl*cyclo*hexane*-3 : 5-*diol*, m. p. 124°, which forms radiating clusters of flat, transparent needles, and gives a *dibenzoyl* derivative, m. p. 84°.

On reducing phenyldihydroresorcin, 1-phenyl*cyclo*hexan-3-ol and 1-phenyl*cyclo*hexane-3 : 5-diol are produced. 1-*Phenyl*cyclo*hexan*-3-*ol*, m. p. 81°, forms radiating clusters of colourless needles. 1-Phenyl*cyclo*hexane-3 : 5-diol (Knoevenagel, A., 1896, i, 289) has m. p. 160°; the *dibenzoyl* derivative forms transparent needles containing solvent of crystallisation, and on hydrolysis gives the original phenyl*cyclo*hexanediol, m. p. 160°. A second variety of 1-phenyl*cyclo*hexane-3 : 5-diol, probably the *cis*-form, m. p. 134°, is also obtained in small quantities; it forms nacreous, scaly needles, and yields a *dibenzoyl* derivative, m. p. 117°, which crystallises in silky needles and on hydrolysis is reconverted into the diol, m. p. 134°. E. G.

Catalytic Reduction of Organic Halogen Compounds. W. Borsche and G. Heimbürger (*Ber.*, 1915, **48**, 452—458).—According to the accepted views, the catalytic reduction of halogeno-ethylenes consists in the addition of hydrogen followed by the replacement of the halogen, and the latter stage is said to proceed much more slowly than the former (Willstätter and Hatt, A., 1912, i, 545; Ott, A., 1913, i, 825). This being so, it was hoped that ω-halogenostyrenes could be reduced to ω-halogenoethylbenzenes which would be useful for synthetic purposes. It was found, however, that halogen-free compounds were always obtained forthwith. This could happen according to the scheme:

$$Ar\cdot CH{:}CHX \xrightarrow{+H_2} Ar\cdot CH_2\cdot CH_2X \xrightarrow{-HX} Ar\cdot CH{:}CH_2 \longrightarrow Ar\cdot CHMe,$$

but benzyl and benzylidene chlorides give toluene by catalytic reduction and, therefore, the conclusion must be drawn, that under certain conditions halogens may be directly substituted by hydrogen during the hydrogenation.

Piperonylacrylic acid was dissolved in potassium carbonate, mixed with potassium hypochlorite at 0°, and then submitted to a slow stream of carbon dioxide, when ω-*chlorovinyl*-3 : 4-*methylenedioxybenzene* [*α-chloro-β-piperonylethylene*], $CH_2{:}O_2{:}C_6H_3\cdot CH{:}CHCl$, separated in colourless needles, m. p. 29—30°. This was reduced by colloidal palladium and hydrogen to ethylcatechol methylene ether, b. p. 213° (Klages and Eppelsheim, A., 1904, i, 45).

ω-*Chloro*-p-*methoxystyrene*, $OMe\cdot C_6H_4\cdot CH{:}CHCl$, was prepared in the same way from *p*-methoxycinnamic acid, in colourless leaflets, m. p. 34°, and was reduced to *p*-methoxyethylbenzene, b. p. 195—196° (*ibid.*). The reduction seemed to be favoured by alcohol, for it took four times as long in acetone.

ω-Bromostyrene gave ethylbenzene; benzylidene chloride gave toluene and a small amount of *s*-dichlorodiphenylethane,

$$CHPhCl\cdot CHPhCl;$$

whilst benzotrichloride gave *s*-tetrachlorodiphenylethane. J. C. W.

Polyhydric Mercaptans of the Benzene Series. IV. Sulphonation of Thiophenolic Ethers. J. POLLAK (*Monatsh.*, 1914, **35**, 1445—1465. Compare A., 1914, i, 39).—Methyl ethers of polyhydric phenols have been prepared by sulphonating methylthiolbenzene and *m*-dimethylthiolbenzene, and reducing the sulphonyl chlorides with tin and hydrochloric acid. Thus, methylthiolbenzene on treatment with fuming sulphuric acid yields a mixture of 1-methylthiolbenzene-2 : 4-disulphonic and *p*-methylthiolbenzenesulphonic acids, the chlorides of which are reduced to 2 : 4-dithiol-1-methylthiolbenzene and 4-thiol-1-methylthiolbenzene respectively.

[With A. WIENERBERGER.]—1-*Methylthiolbenzene*-2 : 4-*disulphonyl chloride*, $SMe{\cdot}C_6H_3(SO_2Cl)_2$, is prepared from the mixture of mono- and di-sulphonic acids mentioned above by heating the potassium salts with phosphorus pentachloride at 150° and extracting the resulting chlorides with ether. It is less soluble than the mono-sulphonyl chloride and crystallises in stellar aggregates of white needles, m. p. 103—106°. On reduction with tin and hydrochloric acid it yields 2 : 4-*dithiol*-1-*methylthiolbenzene*, $SMe{\cdot}C_6H_3(SH)_2$, as a yellow oil, b. p. 182—184°/16 mm.

The latter compound is oxidised by hydrogen peroxide in ammoniacal alcoholic solution to a pale yellow, amorphous *substance*, probably $(SMe{\cdot}C_6H_3S_2)_n$, insoluble in all organic media. It forms a *diacetyl* derivative, $SMe{\cdot}C_6H_3(SAc)_2$, crystallising in white flakes, m. p. 62—66°, and reacts with chloroacetic acid in alkaline solution, yielding 1-*methylthiolbenzene*-2 : 4-*dithiolacetic acid*, $SMe{\cdot}C_6H_3(S{\cdot}CH_2{\cdot}CO_2H)_2$, which crystallises from water in a felted, asbestos-like mass of lustrous, silky needles, m. p. 157—160°. With chloro-2 : 4 : 6-trinitrobenzene it yields 1-*methylthiol*-2 : 4-*di*-2′ : 4′ : 6′-*trinitrophenylthiolbenzene*,

$$SMe{\cdot}C_6H_3[S{\cdot}C_6H_2(NO_2)_3]_2.$$

This has m. p. 228—231°, and separates from glacial acetic acid in crystals containing 2 mols. of the solvent.

1 : 2 : 4-*Trimethylthiolbenzene*, $C_6H_3(SMe)_3$, prepared by methylating 2 : 4-dithiol-1-methylthiolbenzene with methyl sulphate and aqueous potassium hydroxide, forms hemispherical clusters of soft, white needles, m. p. 49—53°.

The yellow, oily chloride obtained by evaporating the ethereal extract from the 1-methylthiolbenzene-2 : 4-disulphonyl chloride consists mainly of *p*-methylthiolbenzenesulphonyl chloride, and on reduction with tin and hydrochloric acid undergoes partial demethylation with the formation of *p*-dithiolbenzene and *o*(?)-thiolmethylthiolbenzene, $SMe{\cdot}C_6H_4{\cdot}SH$, which was isolated in the form of its 2 : 4 : 6-*trinitrophenyl* derivative, $SMe{\cdot}C_6H_4{\cdot}S{\cdot}C_6H_2(NO_2)_3$, dark red crystals, m. p. 144—147°.

The author inclines to the view that this trinitrophenyl derivative is an ortho-compound, whilst the trinitrophenyl derivative, m. p. 178—180°, described below represents the para-isomeride, but whether the ortho-compound owes its formation to the presence of *o*-methylthiolbenzenesulphonic acid in the original mixture of sulphonic acids could not be determined.

The interaction of methylthiolbenzene and sulphuric acid yields a monosulphonic acid, which forms a *potassium* salt crystal-

lising in pearly flakes, and consists mainly, if not entirely, of *p*-methylthiolbenzenesulphonic acid. Reduction of the corresponding sulphonyl chloride results in the formation of a mercaptan mixture, which is converted by methyl sulphate and aqueous potassium hydroxide into 1 : 4-dimethylthiolbenzene, and on treatment with chloro-2 : 4 : 6-trinitrobenzene in alcoholic solution gives rise to *p*-di-2 : 4 : 6-trinitrophenylthiolbenzene and p(?)-*methylthiol*-2 : 4 : 6-*trinitrophenylthiolbenzene*, $SMe\cdot C_6H_4\cdot S\cdot C_6H_2(NO_2)_3$, crystallising in slender, pale yellow needles, m. p. 178—180°.

p-*Di*-2 : 4 : 6-*trinitrophenylthiolbenzene*, $C_6H_4[S\cdot C_6H_2(NO_2)_3]_2$, prepared from *p*-dithiolbenzene and chloro-2 : 4 : 6-trinitrobenzene in alcoholic solution, has m. p. 263—266°; the meta-*isomeride* crystallises in lustrous, orange scales, m. p. 207—211°.

[With B. SCHADLER.]—1 : 3-*Dimethylthiolbenzene*-4 : 6-*disulphonic acid*, prepared by sulphonating *m*-dimethylthiolbenzene, forms a *chloride*, $C_6H_2(SMe)_2(SO_2Cl)_2$, crystallising in small, white leaflets (decomp. 170—176°). The constitution of the chloride has been established by its conversion into 1 : 3 : 4 : 6-tetrachlorobenzene when heated with thionyl chloride.

4 : 6-*Dithiol*-1 : 3-*dimethylthiolbenzene*, $C_6H_2(SMe)_2(SH)_2$, obtained by reducing the chloride with zinc dust and hydrochloric acid, forms greenish-yellow, felted needles, m. p. 78—81°, and is oxidised by hydrogen peroxide in alcoholic ammoniacal solution to a yellow amorphous *substance*, $(C_6H_2[SMe]_2S_2)_n$, m. p. 220° with previous sintering at 65°. It reacts with chloroacetic acid and with methyl sulphate in alkaline solution, yielding 1 : 3-*dimethylthiolbenzene*-4 : 6-*dithiolacetic acid*, $C_6H_2(SMe)_2(S\cdot CH_2\cdot CO_2H)_2$, small, white needles, m. p. 189—192°, and 1 : 3 : 4 : 6-*tetramethylthiolbenzene*, $C_6H_2(SMe)_4$, long, yellow needles, m. p. 123—127°, respectively.

The *diacetyl* derivative crystallises in pearly, lustrous plates, m. p. 153—156°; the *di*-2 : 4 : 6-*trinitrophenyl* derivative,

$$C_6H_2(SMe)_2[S\cdot C_6H_2(NO_2)_3]_2,$$

separates from glacial acetic acid in shimmering, pale yellow scales, m. p. 242—248°, containing two molecules of the solvent. F. B.

Polyhydric Mercaptans of the Benzene Series. V. Substituted *m*-Dithiolbenzenes. J. POLLAK and A. WIENERBERGER (*Monatsh.*, 1914, **35**, 1467—1491).—A further extension of the method, described in the preceding abstract, of preparing polyhydric mercaptans by the reduction of the corresponding sulphonyl chlorides.

1 : 3-*Dichlorobenzene*-4 : 6-*disulphonyl chloride*, $C_6H_2Cl_2(SO_2Cl)_2$, prepared by the interaction of phosphorus pentachloride and the potassium salt of resorcinoldisulphonic acid (Fischer, A., 1881, 1147), crystallises in short, stout, white needles, m. p. 122—123°. The position of the substituents has been established by the formation of 1 : 3 : 4 : 6-tetrachlorobenzene when the sulphonyl chloride is heated with thionyl chloride at 170°. The chloride is reduced by tin and hydrochloric acid to 1 : 3-*dichloro*-4 : 6-*dithiolbenzene*, $C_6H_2Cl_2(SH)_2$. This crystallises in white scales or stout, pale yellow needles, m. p. 113—115°, and yields a *diacetyl* derivative, crystallising in long needles, m. p. 64—67°. It reacts with chloroacetic acid and with

ethyl chlorocarbonate in alkaline solution to form 1 : 3-*dichlorobenzene*-4 : 6-*dithiolacetic acid*, $C_6H_2Cl_2(S\cdot CH_2\cdot CO_2H)_2$, white, asbestos-like, silky needles, m. p. 200—204°, and 1 : 3-*dichloro*-4 : 6-*diethylthiocarbonatobenzene*, $C_6H_2Cl_2(S\cdot CO_2Et)_2$, white, rectangular leaflets having a pearly lustre, m. p. 50—52°, respectively.

With chloro-2 : 4 : 6-trinitrobenzene in alcoholic solution it yields 1 : 3-*dichloro*-4 : 6-*di*-2′ : 4′ : 6′-*trinitrophenylthiolbenzene*,

$$C_6H_2Cl_2[S\cdot C_6H_2(NO_2)_3]_2,$$

small, vivid yellow needles, m. p. 272—274°, and on methylation with methyl sulphate is converted into 1 : 3-dichloro-4 : 6-dimethylthiol benzene (Zincke and Krüger, A., 1913, i, 44).

1 : 3-*Dichloro*-6-*methylthiol*-4-*methylsulphinylbenzene*,

$$SMe\cdot C_6H_2Cl_2\cdot SOMe,$$

prepared by oxidising 1 : 3-dichloro-4 : 6-dimethylthiolbenzene with nitric acid in glacial acetic acid solution, crystallises in tufts of pale yellow needles, m. p. 122—123°; oxidation with fuming nitric acid or with hydrogen peroxide in cold glacial acetic acid solution results in the formation of 1 : 3-*dichloro*-4 : 6-*dimethylsulphinylbenzene*,

$$C_6H_2Cl_2(SOMe)_2,$$

lustrous, pearly scales, m. p. 264—266°. That the last-named compound is a disulphoxide and not a sulphone is shown by its ready reconversion into the parent substance by hydrobromic acid.

1 : 3-*Dichloro*-4 : 6-*dimethylsulphonylbenzene*, $C_6H_2Cl_2(SO_2Me)_2$, prepared by oxidising 1 : 3-dichloro-4 : 6-dimethylthiolbenzene with hydrogen peroxide in hot glacial acetic acid solution, crystallises in long, white needles, m. p. 236—238°. On treatment with chlorine in chloroform solution, 1 : 3-dichloro-4 : 6-dithiolbenzene gives rise to 1 : 3-dichloro-4 : 6-dichlorothiolbenzene, m. p. 95—97° (Zincke and Krüger, *loc. cit.*, give 103°); oxidation with hydrogen peroxide in alcoholic ammoniacal solution yields a substance, $(C_6H_2Cl_2S_2)_n$, identical with that obtained by Zincke and Krüger by the action of alcohol or strong alkalis on 1 : 3-dichloro-4 : 6-dichlorothiolbenzene.

1 : 3-*Dimethoxybenzene*-4 : 6-*disulphonic acid*, $C_6H_2(OMe)_2(SO_3H)_2$, obtained (1) by directly sulphonating resorcinol dimethyl ether or (2) by the action of methyl sulphate and aqueous potassium hydroxide on potassium 1 : 3-dihydroxybenzene-4 : 6-disulphonate and subsequent hydrolysis of the resulting ester, forms a *potassium* salt, crystallising in small, pale yellow, oblique prisms. The *chloride*,

$$C_6H_2(OMe)_2(SO_2Cl)_2,$$

forms strongly refractive, pale yellow crystals, m. p. 175—178°, belonging to the rhombic system ($a : b : c = 0{\cdot}9228 : 1 : 0{\cdot}9179$), and on reduction with tin and hydrochloric acid is converted into a mixture of 1 : 3-dimethoxy-4 : 6-dithiolbenzene, 1 : 3-dimethoxy-4-thiolbenzene, and *m*-dimethoxybenzene.

1 : 3-*Dimethoxy*-4 : 6-*dithiolbenzene*, $C_6H_2(OMe)_2(SH)_2$, is best prepared by reducing 1 : 3-dimethoxybenzene-4 : 6-disulphonyl chloride with zinc dust and hydrochloric acid in alcoholic solution. It crystallises in pale yellow rosettes, m. p. 89—92°, b. p. 189—190°/20 mm., forms a *diacetyl* derivative, lustrous, silvery scales, m. p. 168—172°, and is oxidised by hydrogen peroxide in alcoholic ammoniacal solution to an amorphous *substance*, $[C_6H_2(OMe)_2S_2]_n$.

With chloroacetic acid and methyl sulphate in alkaline solution it yields 1 : 3-*dimethoxybenzene*-4 : 6-*dithiolacetic acid*, $C_6H_2(OMe)_2(S\cdot CH_2\cdot CO_2H)_2$, slender needles, m. p. 158—160°, and 1 : 3-*dimethoxy*-4 : 6-*dimethylthiolbenzene*, $C_6H_2(OMe)_2(SMe)_2$, pale yellow needles, having a silky lustre, m. p. 83—86°.

1 : 3-*Dimethoxy*-4-*thiolbenzene*, $C_6H_3(OMe)_2\cdot SH$, obtained by the reduction of 1 : 3-dimethoxybenzene-4 : 6-disulphonyl chloride with tin and hydrochloric acid, is a strongly refractive, pale yellow oil, b. p. 159—160°/20 mm., yields on oxidation with hydrogen peroxide the *substance* $[C_6H_3(OMe)_2S]_n$ as a yellowish-white powder and reacts with chloroacetic acid and with methyl sulphate in alkaline solution to form 1 : 3-*dimethoxybenzene*-4-*thiolacetic acid*, $C_6H_3(OMe)_2\cdot S\cdot CH_2\cdot CO_2H$, white crystals, m. p. 92—96°, and 1 : 3-*dimethoxy*-4-*methylthiolbenzene*, $C_6H_3(OMe)_2\cdot SMe$, white, silky, lustrous needles, m. p. 33—37°, respectively. The *acetyl*, m. p. 48—66° (not sharp), and 2 : 4 : 6-*trinitrophenyl* derivatives, $C_6H_3(OMe)_2\cdot S\cdot C_6H_2(NO_2)_3$, red needles, m. p. 147—148°, are also described. F. B.

5-Thiol-α-naphthol. H. Rennert (*Ber.*, 1915, **48**, 459—470).—The preparation and properties of compounds very similar to the derivatives of 4-thiol-α-naphthol (Zincke and Ruppersberg, this vol., i, 135) are described.

A solution of the technical sodium α-naphthol-5-sulphonate was clarified by freshly precipitated lead sulphide and then shaken with ethyl chlorocarbonate, which formed *sodium* 1-*ethylcarbonatonaphthalene*-5-*sulphonate*, $C_{13}H_{11}O_6SNa$, in colourless needles. This was converted into the *sulphonyl chloride*, $CO_2Et\cdot O\cdot C_{10}H_6\cdot SO_2Cl$, long needles, m. p. 79°, which yielded the *anilide*, leaflets, m. p. 129°, and was also reduced by zinc dust and hydrochloric acid to 1-*ethylcarbonato*-5-*thiolnaphthalene*, $SH\cdot C_{10}H_6\cdot O\cdot CO_2Et$. This separated in colourless crystals, m. p. 41—42°, formed an *acetyl* derivative, $C_{15}H_{14}O_4S$, long, silky needles, m. p. 86°, and was oxidised by ferric chloride in alcohol to *αα'-diethylcarbonatonaphthyl* 5 : 5'-*disulphide*, $(CO_2Et\cdot O\cdot C_{10}H_6)_2S_2$, m. p. 87°. It was also methylated by methyl sulphate to the *compound*, $CO_2Et\cdot O\cdot C_{10}H_6\cdot SMe$, m. p. 79°, which yielded with bromine in acetic acid a *brominated perbromide*, $C_{14}H_{13}O_3Br_3S$, reddish-brown needles, m. p. 103° (decomp.), and this was converted into the *sulphoxide*, $CO_2Et\cdot O\cdot C_{10}H_5Br\cdot SOMe$ (bromine probably in 4), long needles, m. p. 119—120°. It did not give a sulphoxide on oxidation with concentrated hydrogen peroxide, but the 1-*ethylcarbonatonaphthyl*-5-*methylsulphone*, $CO_2Et\cdot O\cdot C_{10}H_6\cdot SO_2Me$, glistening needles, m. p. 94—95°.

The ethylcarbonatothiolnaphthalene also reacted with benzyl chloride to give 5-α-*ethylcarbonatonaphthyl benzyl sulphide*, $CO_2Et\cdot O\cdot C_{10}H_6\cdot S\cdot CH_2Ph$, colourless leaflets, m. p. 136—137°. This was converted into the above sulphonyl chloride, m. p. 79°, by the action of chlorine in acetic acid, and was oxidised to the *sulphone*, $C_{20}H_{18}O_5S$, slender needles, m. p. 130°, by perhydrol.

The ethylcarbonatomercaptan was also hydrolysed, by boiling with dilute sodium hydroxide and a little sodium sulphide, to 5-*thiol*-α-

naphthol, $SH\cdot C_{10}H_6\cdot OH$, which forms glistening needles, m. p. 131—132°, and yields a *diacetate*, m. p. 149—150°. The other ethylcarbonato-derivatives were also hydrolysed. *5-α-Hydroxynaphthyl methyl sulphide* [*5-methylthiol-α-naphthol*], $OH\cdot C_{10}H_6\cdot SMe$, forms transparent needles, m. p. 154—155°: its *acetate* has m. p. 77—78°, and its *methyl ether*, $OMe\cdot C_{10}H_6\cdot SMe$, crystallises in silvery leaflets, m. p. 134°. *α-Naphthol-5-methylsulphone*, $OH\cdot C_{10}H_6\cdot SO_2Me$, forms white needles, m. p. 163°. *5-α-Hydroxynaphthyl benzyl sulphide* [*5-benzylthiol-α-naphthol*], $OH\cdot C_{10}H_6\cdot S\cdot CH_2Ph$, crystallises in silky needles, m. p. 130°, and its *acetate* in glistening leaflets, m. p. 157°. *α-Naphthol-5-benzylsulphone*, $OH\cdot C_{10}H_6\cdot SO_2\cdot CH_2Ph$, has m. p. 234°, and its *acetate*, m. p. 118°. *α-Naphthol-5-sulphinic acid*, $OH\cdot C_{10}H_6\cdot SO_2H$, was prepared by gradually adding a mixture of the above ethylcarbonatosulphonyl chloride with sodium hydrogen carbonate to a warm solution of sodium sulphite. It decomposes above 120°, yields the above α-naphthol-5-methylsulphone by the action of methyl iodide on the silver salt, and the *methyl ether* of this, $OMe\cdot C_{10}H_6\cdot SO_2Me$, silky needles, m. p. 98°, when shaken with methyl sulphate in alkaline solution.

When the 5-α-ethylcarbonatonaphthyl benzyl sulphide and the 1-ethylcarbonato-5-thiolnaphthalene are saturated with chlorine in cold chloroform they form the same sulphur-free compound, probably *2 : 4 : 5 : 6 : 8-pentachloro-1-ethylcarbonatonaphthalene*, $C_{13}H_7O_3Cl_5$, long needles, m. p. 129—130°, which is converted by cold alcoholic potassium hydroxide into the *compound*, $C_{10}H_5O_3Cl_3$, m. p. 172°. α-Ethylcarbonatonaphthalene yields a similar *compound*, $C_{13}H_8O_3Cl_4$, m. p. 126—127°. J. C. W.

The Valency of Sulphur. H. Lecher (*Ber.*, 1915, **48**, 524—536).—The aromatic disulphides, $ArS\cdot SAr$, are somewhat analogous in structure to the hexa-arylethanes, $Ar_3C\cdot CAr_3$. It seemed, therefore, to be of interest to test whether the disulphides show any tendency to dissociate into free radicles. Such dissociation has also been observed in the cases of nitrogen (in tetra-arylhydrazines, Wieland, A., 1912, i, 902) and oxygen (in some aromatic peroxides, Pummerer and Cherbuliez, this vol., i, 417), and it was naturally expected that the aromatic nuclei would weaken the union between two sulphur atoms in a similar manner. Diphenyl disulphide and 1 : 1′-bisdimethylaminophenyl 4 : 4′-disulphide,

$$NMe_2\cdot C_6H_4\cdot S\cdot S\cdot C_6H_4\cdot NMe_2,$$

have been examined.

Concentrated solutions of the colourless diphenyl disulphide in indifferent solvents are pale yellow, and the molten substance is also yellow. The colour deepens with rise of temperature and pales again on cooling. This change of colour might be due to dissociation into radicles, thus: $C_6H_5\cdot S\cdot S\cdot C_6H_5 \rightleftarrows 2C_6H_5\cdot S$, but the solutions, both in cold benzene and in boiling xylene, obey Beer's colorimetric dilution law, whereas Piccard has shown (A., 1911, ii, 561) that substances which dissociate in solution do not obey this law. The bisdimethylaminophenyl disulphide behaves similarly. The colour changes are therefore supposed to be due, not to dissociation into free radicles or to rearrangement of the atoms, but to a redistribution of the valencies.

Although the disulphides do not dissociate into free radicles, the link between the sulphur atoms becomes weaker with rise of temperature, for a number of reactions can be brought about which necessitate the fission of the molecule at this point. Thus, diphenyl disulphide is not affected by powdered sodium in cold ethereal solution, is slightly decomposed by sodium potassium alloy in cold petroleum, but may readily be converted into the sodium salt of phenyl mercaptan, $C_6H_5 \cdot SNa$, by shaking a boiling xylene solution with sodium. This method offers the most convenient process for the preparation of *p*-dimethylaminophenyl mercaptan, for the disulphide is easily obtained by the action of sulphur chloride on dimethylaniline (Merz and Weith, A., 1886, 792). Lead amalgam also causes the same disruption in boiling xylene.

Both disulphides are quite stable towards oxygen in boiling xylene.

The bisdimethylaminophenyl disulphide reacted in an interesting manner with triphenylmethyl. Boiling toluene solutions of the disulphide and triphenylmethyl slowly became pale, boiling xylene solutions much more quickly, and then a solution of hydrogen chloride in ether precipitated the chloride of some unchanged disulphide (soluble in cold dilute hydrochloric acid), and the insoluble chloride of *4-dimethylaminophenyl triphenylmethyl sulphide*, $NMe_2 \cdot C_6H_4 \cdot S \cdot CPh_3$. The free base was liberated by ammonia and obtained in colourless leaflets, m. p. 146—148°. That the compound is a triphenylmethyl salt of the mercaptan is shown by the formation of triphenylmethylcarbinol sulphate and bisdimethylaminophenyl disulphide (the product of the oxidation of the mercaptan) when the substance is dissolved in concentrated sulphuric acid. When the compound is added to boiling naphthalene it undergoes dissociation, and the solution shows the spectrum of triphenylmethyl.

The analogous phenyl triphenylmethyl sulphide, $SPh \cdot CPh_3$, was obtained by Meyer and Fischer (A., 1911, i, 121) by the action of triphenylchloromethane on phenyl mercaptan. As the resulting hydrogen chloride may have caused the rearrangement of the triphenylmethyl residue, the author has now prepared the compound from the sodium salt. The new preparation coincides with the old description. It also dissociates into triphenylmethyl in boiling ethyl benzoate or molten naphthalene. J. C. W.

The Action of Organo-magnesium Compounds on Methyl *o*- and *p*-Cresotate. H. Berlitzer (*Monatsh.*, 1915, **36**, 191—209).—A contribution towards the knowledge of the action of the Grignard reagent on esters of aromatic hydroxy-acids.

Methyl *o*-cresotate reacts with magnesium ethyl bromide with formation of *2-hydroxy-m-tolyldiethylcarbinol*, $OH \cdot C_6H_3Me \cdot CEt_2 \cdot OH$, leaflets; when heated with sodium acetate and acetic anhydride this substance underwent concurrent acetylation and dehydration, giving *γ-2-acetoxy-m-tolyl-Δ$^{\beta}$-pentene*, $OAc \cdot C_6H_3Me \cdot CEt{:}CHMe$, an oily, colourless liquid, b. p. 124—127°/11 mm., of characteristic odour, which on saponification yielded *γ-2-hydroxy-m-tolyl-Δ$^{\beta}$-pentene*,

$$OH \cdot C_6H_3Me \cdot CEt{:}CHMe,$$

an oil, b. p. 108—112°/13 mm.

Magnesium propyl bromide with the above ester yielded *2-hydroxy-*

m-*tolyldipropylcarbinol*, $OH\cdot C_6H_3Me\cdot CPr_2\cdot OH$, prisms, m. p. 157°, which was converted by sodium acetate and acetic anhydride into δ-2-*acetoxy*-m-*tolyl*-Δ$^{\gamma}$-*heptene*, $OAc\cdot C_6H_3Me\cdot CPr{:}CHEt$, a pleasant smelling oil, b. p. 138—142°/11 mm.; hydrolysis liberated the corresponding phenol, δ-2-*hydroxy*-m-*tolyl*-Δ$^{\gamma}$-*heptene*,

$$OH\cdot C_6H_3Me\cdot CPr{:}CHEt,$$

a colourless oil, b. p. 124—127°/11 mm.

With magnesium benzyl chloride the ester was converted into 2-*hydroxy*-m-*tolyldibenzylcarbinol*, $OH\cdot C_6H_3Me\cdot C(CH_2Ph)_2\cdot OH$, prisms, m. p. 121—122°, which resisted all attempts at dehydration to the corresponding olefine. In a similar manner magnesium phenyl bromide gave rise to 2-*hydroxy*-m-*tolyldiphenylcarbinol*, prisms, m. p. 120—121°, and magnesium α-naphthyl bromide to 2-*hydroxy*-m-*tolyldi*-α-*naphthylcarbinol*, m. p. 214° (decomp.), both of which resisted conversion into the corresponding ethylenic compounds.

Methyl *p*-cresotate reacted with magnesium methyl bromide producing 4-*hydroxy*-m-*tolyldiethylcarbinol*, leaflets, m. p. 81—82°, which was converted in the same manner as its ortho-isomeride into the corresponding γ-4-*acetoxy*-m-*tolyl*-Δ$^{\beta}$-*pentene*, an oil of characteristic odour, b. p. 138—139°/12 mm., and γ-4-*hydroxy*-m-*tolyl*-Δ$^{\beta}$-*pentene*, a pleasant smelling oil, b. p. 116—119°/10 mm.

In a similar manner magnesium propyl bromide gave rise successively to 4-*hydroxy*-m-*tolyldipropylcarbinol*, colourless needles, m. p. 84—85°; δ-4-*acetoxy*-m-*tolyl*-Δ$^{\gamma}$-*heptene*, an oil of characteristic odour, b. p. 150—152°/12 mm., and δ-4-*hydroxy*-m-*tolyl*-Δ$^{\gamma}$-*heptene*, a colourless liquid, b. p. 136—138°/11 mm.

Magnesium benzyl chloride converted the para-ester into 4-*hydroxy*-m-*tolyldibenzylcarbinol*, m. p. 111—112°, and magnesium phenyl bromide in like manner produced 4-*hydroxy*-m-*tolyldiphenylcarbinol*, m. p. 166—167°; the latter substance decomposes at its m. p., giving rise to 9-*phenyl*-7-*methylxanthene*, needles, m. p. 145°. The interaction of methyl *p*-cresotate with magnesium α-naphthyl bromide produced 4-*hydroxy*-m-*tolyldi*-α-*naphthylcarbinol*, microscopic crystals, m. p. 184° (decomp.). D. F. T.

Steric Hindrance of Chemical Reactions. III. Chloromethylenedibenzoate. F. Wenzel [and Leo Bellak] (*Monatsh.*, 1914, **35**, 965—971).—Under the influence of aluminium chloride, chloromethylenedibenzoate condenses with benzene, yielding the benzoyl derivative of benzhydrol. Anisole and mesitylene, on the other hand, are converted into anisaldehyde and 2 : 4 : 6-trimethylbenzaldehyde; dibenzoates of the type, $R\cdot CH(OBz)_2$, are probably formed as intermediate products during the reaction, but all attempts to isolate them proved unsuccessful.

Chloromethylenedibenzoate, $CHCl(OBz)_2$, prepared by chlorinating methylenedibenzoate in benzene solution at the ordinary temperature, has m. p. 96°, and is quantitatively hydrolysed by hot alcoholic potassium hydroxide to benzoic and formic acids. In the presence of aluminium chloride it readily reacts with mesitylene in benzene solution, yielding 2 : 4 : 6-*trimethylbenzaldehyde* as an oil, b. p. 192°/50 mm.

Anisylidene dibenzoate, prepared by heating anisaldehyde with benzoic anhydride, has m. p. 119°. F. B.

The Walden Inversion. I. Influence of the Solvent on the Sign of the Product in the Conversion of Phenylchloroacetic Acid to Phenylaminoacetic Acid. GEORGE SENTER and HARRY DUGALD KEITH DREW (T., 1915, **107**, 638—642).—By the interaction of the ammonium salts of *d*- or *l*-phenylchloroacetic acid with ammonia in aqueous solution, phenylaminoacetic acid is obtained, which has the opposite sign to that of the chloro-substituted acid. The authors have found that if acetonitrile is used as solvent instead of water, the resulting amino-acid has the same sign as the phenylchloroacetic acid used in the reaction. Experiments have been made with both the *d*- and *l*-acids with the same result. In both solvents there is considerable racemisation, but whereas the proportion of active acid in the product decreases with rise of temperature when water is used as the reactive medium, the proportion of the active amino-acid is practically independent of the temperature (between 9° and 52°) when reaction occurs in acetonitrile.

The results are considered to show that one or both of the solvents participate in the reaction. H. M. D.

Action of Sunlight on the Cinnamic Acids. A. W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1274—1277).—It has been shown previously that the action of sunlight on *allo*-cinnamic acid gives rise to α- and β-truxillic and normal cinnamic acids (compare A., 1911, i, 639). Since the addition of normal cinnamic acid to the *allo*-acid increased the quantity of β-truxillic acid, it was supposed that β-truxillic acid is formed by the combination of one molecule of *allo*-acid with one molecule of normal acid. Further experiments have shown that this is not the case.

Comparative experiments were made in which equal quantities of (1) *allo*-cinnamic acid, (2) normal cinnamic acid, (3) a 50% mixture of the two acids were exposed to sunlight and the quantities of α- and β-truxillic acids formed were determined. The results obtained show that both α- and β-truxillic acids are formed from the normal cinnamic acid much more readily than from the *allo*-acid. From experiments in which normal cinnamic acid was exposed to sunlight in the form of (*a*) a fine powder, (*b*) crystals, it has been found that the finely divided condition of the acid prevents the formation of β-truxillic acid, and in this manner an explanation is obtained of Riiber's experiments (A., 1902, i, 785) in which no β-truxillic acid was formed by the action of sunlight on cinnamic acid. H. M. D.

Salicylates; Salicylates of Lead and Copper. W. OECHSNER DE CONINCK (*Bull. Soc. chim.*, 1915, [iv], **17**, 164—167. Compare A., 1914, i, 957, 1070).—By treating lead salicylate with boiling aqueous ammonia the author was unable to obtain the basic salicylate, $(C_7H_4O_3)_2Pb_2,3PbO$, but obtained a mixture of basic salts varying with the temperature and time of heating. When the normal salicylate is heated slowly and progressively with an equimolecular

proportion of litharge the basic salt, $C_6H_4<^{CO_2}_{O-}>Pb$, is obtained together with a small amount of lead hydroxy*iso*phthalate.

By adding copper sulphate to calcium salicylate, copper salicylate was obtained as a dihydrate on the addition of alcohol followed by rapid concentration on a water-bath. This salicylate is easily decomposed by water, alcohol or ether at a moderate temperature, giving the basic salicylate, $C_6H_4<^{CO_2}_{O-}>Cu$.

The comparatively stable salicylates are decomposed at moderately high temperatures to basic salicylate, $C_6H_4<^{CO_2}_{O-}>M''$, phenol and carbon dioxide, whilst the unstable salicylates are decomposed at lower temperatures by water, alcohol or ether, giving a similar basic salicylate and salicylic acid. W. G.

Some Basic Salicylates. W. Oechsner de Coninck and Gérard (*Compt. rend.*, 1915, **160**, 627—628).—The authors have prepared salts from a number of substituted salicylic acids, to see if the latter, like salicylic acid itself, would furnish basic salts of the type

$$C_6H_4<^{CO_2}_{O-}>M''.$$

The following are described: Basic *lead bromosalicylate*,

$$C_6H_3Br<^{CO_2}_{O-}>Pb,H_2O,$$

is obtained by the interaction of barium bromosalicylate and lead acetate. Basic *lead dibromosalicylate*, $C_6H_2Br_2<^{CO_2}_{O-}>Pb$, is similarly obtained. Normal barium chlorosalicylate when left in contact with dilute ammonia for two to three hours yields basic *barium chlorosalicylate*, $C_6H_3Cl<^{CO_2}_{O-}>Ba,H_2O$. *Lead aminosalicylate*,

$$NH_2\cdot C_6H_3<^{CO_2}_{O-}>Pb,$$

is precipitated by ammonia from a solution of the normal salt. *Lead sulphosalicylate*, $HO\cdot C_6H_3<^{SO_3}_{CO_2}>Pb,PbO$, is obtained by digesting the acid with freshly precipitated lead oxide. Basic *barium iodosalicylate*, $C_6H_3I<^{CO_2}_{O-}>Ba$, and basic *barium di-iodosalicylate*, $C_6H_2I_2<^{CO_2}_{O-}>Ba$, are obtained by treating the corresponding normal salts with ammonia, and basic *barium nitrosalicylate*,

$$NO_2\cdot C_6H_3<^{CO_2}_{O-}>Ba,$$

is similarly prepared. Basic *copper salicylate*, $C_6H_4<^{CO_2}_{O-}>Cu,H_2O$, is obtained by the action of ether on the normal salt. When heated at 97—98° in a current of dry nitrogen the anhydrous salt is obtained. All these basic salts are amorphous and practically insoluble in water. When dried and calcined they soon char. On warming the damp

salt an odour of phenol is evolved, the oxide of the metal being formed,

$$C_6H_4<\begin{matrix}CO_2\\O\end{matrix}>Cu + H_2O = C_6H_5\cdot OH + CuO + CO_2.$$

W. G.

Basic Mercuric Salicylate and Methylsalicylate; their Constitution. Mercuric Anisate. The Mercuric *m*- and *p*-Hydroxybenzoates. H. Lajoux (*J. Pharm. Chim.*, 1915, [vii], **11**, 279—285. Compare A., 1893, i, 642).—A confirmation of Buroni's views (compare A., 1903, i, 256, 392) that the constitution of the basic mercuric salicylate, previously described by the author, is best represented by the formula $OH\cdot C_6H_3<\begin{matrix}CO\\Hg\end{matrix}>O$ (compare Dimroth, A., 1899, i, 428; and Pesci, A., 1903, i, 220). To prove that the mercury has not replaced the hydrogen atom of the hydroxyl group the author has started with *o*-methoxybenzoic acid. The sodium salt of this acid reacts in aqueous solution with a mercuric salt in the cold, giving *mercuric o-methoxybenzoate*, $(OMe\cdot C_6H_4\cdot CO_2)_2Hg$, which on boiling with water gives a *compound*, that does not give the ordinary reactions for mercury. This compound is also obtained by the action of *o*-methoxybenzoic acid in excess on either yellow mercuric oxide or mercuric acetate in boiling water. The only possible constitution for this compound is given by the formula $OMe\cdot C_6H_3<\begin{matrix}CO\\Hg\end{matrix}>O$. The compound is insoluble in sodium hydroxide, ammonium sulphide or potassium cyanide solutions, but is soluble in chloroform. Anisic acid in the cold similarly gives *mercuric anisate*, but on boiling with water is not converted into a basic compound. It does, however, yield a similar basic *compound* if the temperature is raised to 140—150°. The author considers that, in the compound obtained from *o*-methoxybenzoic acid, the mercury is attached to the ring at position 4, whilst in the case of the compound obtained from anisic acid it is attached at some other point, possibly 3. Attempts were made to prepare similar compounds from *m*- and *p*-hydroxybenzoic acids, but the reactions were complicated by the greater strength of the phenolic group in these cases. *m*-Hydroxybenzoic acid did give a *compound*,

$$OH\cdot C_6H_3<\begin{matrix}CO\\Hg\end{matrix}>O,$$

but from *p*-hydroxybenzoic acid a mixture of substances was obtained.

W. G.

Molecular Compounds of Inorganic Haloids. VI. Action of Titanium Tetrachloride on Organic Compounds Containing Oxygen. Arthur Rosenheim [with Richard Schnabel and Robert Bilecki] (*Ber.*, 1915, **48**, 447—452).—In the earlier papers (1901—1905) the author described many additive compounds of the haloids of antimony, silicon, titanium, tin, thorium, platinum and other elements with organic oxy-compounds, and a number of co-workers have since described, in their dissertations, compounds of titanium tetrachloride which are closely related to those obtained by Hauser and Levite (this vol., i, 139). Some of the results have now been assembled.

Salicylic acid and titanium tetrachloride or bromide give the compounds, $TiCl(O{\cdot}C_6H_4{\cdot}CO_2H)_3$, HCl(HBr) (A., 1905, i, 731), which are constituted like the derivatives of 1 : 3-diketones obtained by Dilthey (A., 1904, i, 290; 1906, i, 342). Methyl salicylate gives a derivative of hydrochlorotitanic acid, namely, the ruby-red *compound*,

$$[Ti(O{\cdot}C_6H_4{\cdot}CO_2Me)_3]_2TiCl_6;$$

the ethyl analogue and the corresponding salicylaldehyde derivative are purple (Dilthey). When the above salicylic acid compound is heated at 140—150° it is converted into titanium salicylate which is the anhydride of the acid, $TiO(O{\cdot}C_6H_4{\cdot}CO_2H)_2$, for it combines directly with pyridine in alcohol to give the salt, $TiO(O{\cdot}C_6H_4{\cdot}CO_2{\cdot}C_5H_6N)_2$. The same salicylic acid compound reacts with pyridine in alcohol to give the salt which Hauser and Levite regarded as derived from oxydititanihexasalicylic acid, but which the author prefers to formulate thus: $C_6H_4\langle{}^{O}_{CO_2}\rangle Ti(O{\cdot}C_6H_4{\cdot}CO_2{\cdot}C_5H_6N)_2$.

m- and *p*-Hydroxybenzoic acids do not give definite compounds with titanium tetrachloride, for the ortho-hydroxyl group seems to be an essential (compare Hauser and Levite). *m*-Cresotic acid yields the purple *compound*, $TiCl(O{\cdot}C_6H_3Me{\cdot}CO_2H)_3,HCl$, which combines with pyridine to form the orange *salt*,

$$C_6H_3Me\langle{}^{O}_{CO_2}\rangle Ti(O{\cdot}C_6H_3Me{\cdot}CO_2{\cdot}C_5H_6N)_2,$$

and is converted by heat into the brick-red *titanium cresotate*,

$$Ti(O{\cdot}C_6H_3Me{\cdot}CO_2)_2.$$

J. C. W.

Chromisalicylic Acid and its Ammoniacal Derivatives. G. A. Barbieri (*Atti R. Accad. Lincei*, 1915, **24**, i, 605—610).—The interaction of chrome alum and an alkali salicylate yields chromisalicylic acid (annexed formula), analogous to the ferrisalicylates described by Weinland and Herz (A., 1913, ii, 1189). Solutions of the acid in concentrated ammonia solution gradually deposit, in reddish-violet, microscopic needles, a compound of chromisalicylic acid with $3NH_3(+3H_2O)$. Treatment of this compound with sodium or potassium chloride or silver nitrate results in the replacement of one ammonium group by an atom of the univalent metal. Since the co-ordination number of chromium is six and chromium usually forms compounds which are co-ordinatively saturated, and since further the above silver derivative is anhydrous, it must be assumed that a secondary valency acts between the chromium atom and the carboxyl group connected with the alkali metal (annexed formula). The ammoniacal derivatives of chromisalicylic acid are, therefore, of the type of tetra-acidodiammino-salts, and, in accordance with Werner's system of nomenclature, would be named disalicylato-diamminechromates. They correspond completely with the diammine-chromodioxalates, $[Cr(NH_3)_2(C_2O_4)_2]R$, described by Clève (*K. Vet.*

Akad. Handl., 1865, **6**, 24) and by Pfeiffer and Basci (A., 1906, ii, 616), and with Sörensen's diamminecobaltodioxalates.

The results of analysis of chromisalicylic acid may be represented by the formula given above or by

$$[Cr_3(OH)_2(OH\cdot C_6H_4\cdot CO_2)_6][Cr(O\cdot C_6H_4\cdot CO_2)_2],10H_2O,$$

and the data available are insufficient to decide between these two structures. An iron compound of the latter type was described by Weinland and Herz (*loc. cit.*).

Chromisalicylic acid is a yellow powder and dissolves in alkali hydroxide or carbonate solution with a green coloration, and in ammonia solution or pyridine with a violet coloration.

Ammonium ($+3H_2O$), *potassium* ($+5H_2O$), *sodium* ($+6H_2O$), and *silver diamminechromisalicylates* were prepared and analysed. *Diamminechromisalicylic acid*, $[Cr(NH_3)_2(O\cdot C_6H_4\cdot CO_2)_2]H$, is a red powder, giving a violet solution in dilute aqueous ammonia. T. H. P.

Thioamides. August Albert (*Ber.*, 1915, **48**, 470—473).—Thioamides of acylated α-hydroxy-acids may be obtained by the action of substances which provide hydrogen sulphide on the corresponding nitriles. Alcoholic ammonium sulphide may be used, or thioacetic acid or its ammonium salt if the nitrile contains sensitive groups, such as the nitro-group.

Acetylacetonecyanohydrin, b. p. 180—181°/715 mm., obtained by the action of acetyl chloride on the hydroxycyanide of acetone, was mixed with benzene and saturated with ammonia and then hydrogen sulphide. Next day the solvent was evaporated, and *α-acetoxythioisobutyramide*, $OAc\cdot CMe_2\cdot CS\cdot NH_2$, was obtained in leaflets, m. p. 123°.

3 : 4-Methylenedioxymandelonitrile was prepared by grinding piperonaldehyde with potassium cyanide, covering the mixture with water, and dropping in cold hydrochloric acid. The *acetyl* compound had m. p. 71°, and gave *α-acetoxy-3 : 4-methylenedioxyphenylthioacetamide*, $CH_2{:}O_2{:}C_6H_3\cdot CH(OAc)\cdot CS\cdot NH_2$, needles, m. p. 145°. *Acetylthiomandelamide*, $OAc\cdot CHPh\cdot CS\cdot NH_2$, has m. p. 105°.

α-Acetoxy-*o*-nitrophenylacetonitrile (Heller, A., 1904, i, 416; 1906, i, 585) was boiled with thioacetic acid and benzene, or, better, saturated in benzene with ammonia and hydrogen sulphide at 0° and then shaken with thioacetic acid, and thus converted into *α-acetoxy-o-nitrophenylthioacetamide*, $NO_2\cdot C_6H_4\cdot CH(OAc)\cdot CS\cdot NH_2$, broad tablets, m. p. 145°. The corresponding *benzoyl* derivative forms very regular, rectangular tablets, m. p. 173° (decomp.). J. C. W.

Some Substituted β-Hydroxy-β-phenylpropionic Esters. M. Berberianu (*Bull. Acad. Română*, 1914/5, **3**, 338—343).—The author has prepared a number of substituted β-hydroxy-β-phenylpropionic esters of the type $HO\cdot CPhR\cdot CHR'\cdot CO_2Et$ and

$$HO\cdot CPhR\cdot CR'R''\cdot CO_2Et$$

with the object of studying their behaviour towards Grignard's reagent (compare A., 1914, i, 47).

These esters have been obtained by condensing α-bromoaliphatic esters with benzophenone, and in one case with *p*-methoxybenzophenone

in anhydrous benzene in the presence of magnesium. In this way methyl α-bromopropionate yielded *methyl β-hydroxy-ββ-diphenyl-α-methylpropionate*, $HO\cdot CPh_2\cdot CHMe\cdot CO_2Me$, white crystals, m. p. 128—129°. The corresponding ethyl ester has been prepared by Rupe, Steiger, and Fiedler (compare A., 1914, i, 281). The methyl ester is easily hydrolysed by alcoholic potassium hydroxide in the cold, giving the corresponding acid, m. p. 184°. By condensing benzophenone separately with the ethyl esters of α-bromobutyric, α-bromo*iso*valeric, and α-bromo*iso*butyric acids the author has obtained respectively *ethyl β-hydroxy-ββ-diphenyl-α-ethylpropionate*, m. p. 186—187°; *ethyl β-hydroxy-ββ-diphenyl-α-isopropylpropionate*, m. p. 125—126°, and *ethyl β-hydroxy-ββ-diphenyl-αα-dimethylpropionate*, b. p. 162—164°/12 mm. By condensing methyl α-bromopropionate with *p*-methoxybenzophenone, *methyl β-hydroxy-β-phenyl-β-p-anisyl-α-methylpropionate*, m. p. 124—125°, was obtained. W. G.

o- and *p*-Chlorobenzoylacetic Esters and Some of their Derivatives. LAMBERT THORP and E. R. BRUNSKILL (*J. Amer. Chem. Soc.*, 1915, **37**, 1258—1263).—In continuation of the work on the halogenated benzoylacetic esters (Hale and Thorp, A., 1913, i, 370, 972), a study has been made of the chlorobenzoylacetic esters. It has been found that with regard to ease of alkylation, the chlorobenzoylacetic esters are intermediate between benzoylacetic ester and its nitro-derivatives.

Ethyl o-*chlorobenzoylacetate*, $C_6H_4Cl\cdot CO\cdot CH_2\cdot CO_2Et$, prepared by the action of *o*-chlorobenzoyl chloride on the sodium salt of ethyl acetoacetate, is a pale yellow viscous liquid which cannot be distilled under 30 mm. pressure without decomposition. When boiled with dilute sulphuric acid, it is converted into *o-chloroacetophenone*, b. p. 227—228°/738 mm., n_D^{25} 1·685, D_{25}^{25} 1·1884, a colourless liquid with a pleasant, aromatic odour; this ketone yields an *oxime*, m. p. 103°, which forms silky needles. *2-Chloro-5-nitroacetophenone*, m. p. 62°, crystallises in colourless prisms.

Ethyl p-*chlorobenzoylacetate*, m. p. 38°, forms flat prisms; its *potassium* salt has m. p. 265° (decomp.). p-*Chlorobenzoylacetic acid*, obtained by hydrolysing the ester with dilute potassium hydroxide, melts at 232° when heated rapidly, but when heated slowly, it decomposes with formation of *p*-chloroacetophenone. *Ethyl phenacyl*-p-*chlorobenzoylacetate*, $C_6H_4Cl\cdot CO\cdot CH(CH_2\cdot COPh)\cdot CO_2Et$, m. p. 63°, obtained by the action of phenacyl bromide on the sodium salt of ethyl *p*-chlorobenzoylacetate, forms colourless prisms. The ketonic decomposition of this ester, by means of dilute alkali hydroxide, does not take place so smoothly as that of ethyl benzoylacetate or *o*-chlorobenzoylacetate, but the yield of ketone is diminished by the tendency of the ester to undergo the acid decomposition. *4-Chlorodiphenacyl*,

$$COPh\cdot CH_2\cdot CH_2\cdot CO\cdot C_6H_4Cl,$$

m. p. 114·5°, crystallises in pearly leaflets.

Ethyl p-*chlorophenacylbenzoylacetate*,

$$CHBz(CH_2\cdot CO\cdot C_6H_4Cl)\cdot CO_2Et,$$

m. p. 92°, prepared by the action of *p*-chlorophenacyl bromide on the sodium salt of ethyl benzoylacetate, forms colourless needles; when

hydrolysed with dilute potassium hydroxide, it furnishes 4-chlorodiphenacyl in a yield of 50% of the theoretical. E. G.

Steric Hindrance of Chemical Reactions. I. Mesityl Compounds. F. WENZEL (*Monatsh.*, 1914, **35**, 945—952).—The author finds that whilst mesitylene cannot be brought into reaction with methyl chloroformate by means of the Friedel-Crafts' reaction, it readily undergoes condensation with ethyl chloroglyoxylate and the chloride of ethyl hydrogen malonate, yielding esters of mesitylglyoxylic and 2 : 4 : 6-trimethylbenzoylacetic acid respectively. Since mesitylenecarboxylic acid cannot be directly esterified, whilst mesitylglyoxylic acid is readily transformed into its esters, it would appear that the steric effects which determine this difference in behaviour also come into play during the introduction of negative groups.

Attempts to condense esters of chloroacetic, β-iodopropionic, and bromo*iso*succinic acids with mesitylene by the Friedel-Crafts' reaction were unsuccessful. The failure of the last named substances to enter into reaction is all the more remarkable when it is remembered that the methyl and benzyl groups may be readily introduced in this manner.

[With HANS HELLMANN.]—The methyl and ethyl esters of chloroglyoxylic acid are readily prepared from the oxalic esters by heating with the calculated amount of phosphorus pentachloride at 170° (compare Peratoner and Strazzeri, A., 1891, 1333).

Methyl mesitylglyoxylate, prepared from methyl chloroglyoxylate and mesitylene in the presence of aluminium chloride, is a colourless oil, b. p. 253—255°; the *ethyl* ester has b. p. 265—267°.

Ethyl 2 : 4 : 6-*trimethylbenzoylacetate*, obtained from mesitylene and the semichloride of ethyl oxalate, forms a yellow oil, b. p. 174—176°/12 mm., and is hydrolysed by dilute aqueous potassium hydroxide to the corresponding *acid*, slender needles, m. p. 150—156° (decomp.).

Methyl iso*bromosuccinate*, prepared by direct bromination of methyl succinate, has b. p. 106—108°/12 mm. F. B.

Products of Dehydration of β-Hydroxy-ββ-diphenylpropionic Acid. R. DE FAZI (*Atti R. Accad. Lincei*, 1915, [v], **24**, 729—734).—The action of phosphoric oxide on β-hydroxy-ββ-diphenylpropionic acid gives, not 3-phenylindone (compare following abstract), but *dehydrodi-β-hydroxy-ββ-diphenylpropionic acid*,

$$CO_2H\cdot CH_2\cdot CPh_2\cdot O\cdot CPh_2\cdot CH_2\cdot CO_2H,$$

which forms slender, shining, white needles, m. p. 155—158°, and gives an emerald-green or red coloration with cold or hot concentrated sulphuric acid. The *silver* salt was analysed, and the *ethyl* ester, $C_{34}H_{34}O_5$, which is a dense, red oil, b. p. 210—215°/80 mm., was not obtained quite pure, since it is partly converted into ethyl β-phenylcinnamate on distillation.

The action of sodium acetate and acetic anhydride on β-hydroxy-ββ-diphenylpropionic acid (compare Rupe and Busolt, A., 1908, i, 23) yields β-phenylcinnamic acid and *β-phenylcinnamic anhydride*,

$$O(\cdot CO\cdot CH{:}CPh_2)_2,$$

which forms tufts of white needles, m. p. 118—120°, and gives an

emerald-green or intense red coloration with cold or hot concentrated sulphuric acid. T. H. P.

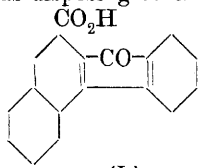
Derivatives of β-Hydroxy-αββ-triphenylpropionic Acid. R. DE FAZI (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 439—442, and *Gazzetta*, 1915, **45**, i, 552—556).—The author has investigated various transformations of the acid obtained by Paternò and Chieffi from benzophenone and phenylacetic acid and regarded by them as β-hydroxy-αββ-triphenylpropionic acid (A., 1911, i, 65).

Attempts to dehydrate the acid by means of phosphoric oxide and so obtain αββ-triphenylacrylic acid resulted in the formation of 2 : 3-diphenylindone (compare Heyl and Meyer, A., 1895, i, 542), the structure suggested by Paternò and Chieffi being thus confirmed. Passage of gaseous hydrogen chloride through an alcoholic solution of β-hydroxy-αββ-triphenylpropionic acid yields *ethyl αβ-diphenylcinnamate* (*αββ-triphenylacrylate*), $CPh_2{:}CPh{\cdot}CO_2Et$, which forms white needles, m. p. 119—120°, and gives with concentrated sulphuric acid an emerald-green coloration becoming orange-red and then ruby-red on heating.

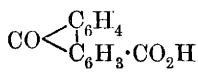
The action of ethyl iodide on silver β-hydroxy-αββ-triphenylpropionate yields, not the corresponding ethyl ester, but a small proportion of a *compound*, which crystallises in colourless, transparent prisms, m. p. 116—119°, contains C 82·49—82·53 and H 6·19—6·25%, and with concentrated sulphuric acid gives an emerald-green coloration, changing to orange, and then to ruby-red on heating; its constitution is being investigated.

An attempt to prepare β-hydroxy-αββ-triphenylpropionic acid by the interaction of benzophenone and ethyl phenylbromoacetate in presence of zinc (compare Rupe and Busolt, A., 1908, i, 23) gave only a product difficult to purify. T. H. P.

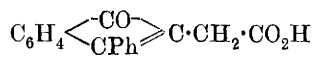
The Colour of Some Cyclic Ketonic Acids and of Their Esters. HANS STOBBE (*Ber.*, 1915, **48**, 441—446).—In an earlier paper (A., 1907, i, 765) the author attempted to explain the contrast between the colours of the deep red, *allo*-chrysoketonecarboxylic acid (I) and its pale yellow ester on the basis of constitutional differences. These compounds, the lemon-yellow fluorenone-4-carboxylic acid (II) and its golden-yellow ester, the orange-yellow phenylindoneacetic acid (III) and its golden-yellow ester, and fluorenone, have now been examined spectrographically, and it is found that, although so different to the eye, they show similar absorption curves and are true ketones, thus disposing of the earlier theories as to their structure.



(I.)



(II.)



(III.)

The chief bands are in the visible spectrum, and near λ 285 μμ and the extreme end of the ultra-violet, the first being typical of the chief chromophore, the half-quinone ring,  . J. C. W.

The Influence of Solvent on the Scission of Carbon Dioxide from Dihydroxybenzoic Acids. FRANZ VON HEMMELMAYR (*Monatsh.*, 1915, **36**, 299—302).—An extension of the investigation of the influence of substituents on the stability of the carboxyl group in substituted hydroxy-acids.

2 : 4-Dihydroxybenzoic acid has been examined as to the ease with which it yields carbon dioxide when boiled with water containing various additions. As has already been stated (von Hemmelmayr, A., 1913, i, 468) the effect of the solvent may be considerably greater than that of temperature. It is now found that in aqueous solution chlorides have a more marked accelerating effect than sulphates, whilst the effect produced by acids generally stands in the relative order of their dissociation. Alkalis increase the stability of the acid, and it is therefore possible that the catalytic effect of mineral acids is due to the elimination of carbon dioxide occurring only with the undissociated 2 : 4-dihydroxybenzoic acid. This view receives confirmation from the fact that a solution of the acid in aniline has a higher electrical conductivity than one in phenol, the latter solvent being more favourable to the decomposition with formation of carbon dioxide. The three isomeric hydroxybenzoic acids appear to exert a slight inhibitory effect on the decomposition in aqueous solution, a behaviour which is also shared by boric acid. D. F. T.

Derivatives of α-Amino-α-methylbutyric Acid and α-Amino-α-ethylbutyric Acid. PAUL FREYTAG (*Ber.*, 1915, **48**, 648—657).—Gabriel (A., 1911, i, 218) showed that α-amino*iso*butyric acid could be converted, through the intervention of the chloride of the phthalimino-acid and the Friedel-Craft's reaction, into α-amino*iso*butyrophenone, $NH_2 \cdot CMe_2 \cdot COPh$. The author has now obtained other ketones of the general formula $NH_2 \cdot CRR' \cdot COPh$ by the same scheme from α-amino-α-methyl(or ethyl)-butyric acids.

These acids were gradually added to molten phthalic anhydride, and the products were ground with cold sodium carbonate solution, which left undissolved the diketopiperazines in about 10% yields. 3 : 6-Diketo-2 : 5-dimethyl-2 : 5-diethylpiperazine had m. p. 340·5° (compare Rosenmund, A., 1910, i, 67), and 3 : 6-*diketo*-2 : 2 : 5 : 5-*tetraethylpiperazine*, $NH<\begin{matrix}CEt_2 \cdot CO \\ CO \cdot CEt_2\end{matrix}>NH$, formed feathery needles, m. p. 346—346·5°. The desired acids crystallised from much water in slender needles. *α-Phthalimino-α-methylbutyric acid*, $C_8H_4O_2{:}N \cdot CMeEt \cdot CO_2H$, had m. p. 141·5—143°, and formed a white *silver* salt, whilst *α-phthalimino-α-ethylbutyric acid* had m. p. 161—162°, and the *silver* salt, m. p. 232° (decomp.).

The latter acid was converted into the *chloride*,

$$C_8H_4O_2{:}N \cdot CEt_2 \cdot COCl,$$

m. p. 73—75°, by means of phosphorus pentachloride. This was shaken with benzene and aluminium chloride, and next day the mass was decomposed by ice and dilute hydrochloric acid, and the solvent was removed by steam. The remaining resin apparently contained the expected α-phthalimino-α-ethylbutyrophenone, for it was hydrolysed by boiling, concentrated hydrochloric acid to phthalic acid and the *hydro-*

chloride of *α-amino-α-ethylbutyrophenone*, $COPh\cdot CEt_2\cdot NH_2,HCl$. About 20% of the resin, however, crystallised readily from alcohol, and was identified as the *lactone* of *1-hydroxy-1-phenylphthalimidyl-α-ethylbutyric acid*, $\begin{matrix}C_6H_4\cdot CPh\text{—}O\\ CO\text{—}N\cdot CEt_2\cdot CO\end{matrix}$, for it was hydrolysed by acetic acid and fuming hydrochloric acid at 133° to benzoylbenzoic and α-amino-α-ethylbutyric acids. The lactone formed flat needles, m. p. 133—134°, and yielded as an intermediate product of hydrolysis (by aqueous-alcoholic potassium hydroxide) an *acid*, $C_{20}H_{21}O_4N$, in platelets, m. p. 201°. This attachment of a benzene nucleus to the phthalic acid residue rather than to the amino-acid group was more complete when the reagents were heated in steam. The resin obtained in this case was extracted by hot ammonia solution and the extracts were acidified, when *1 : 1-diphenylphthalimidyl-α-ethylbutyric acid*, $\begin{matrix}C_6H_4\cdot CPh_2\\ CO\text{—}N\cdot CEt_2\cdot CO_2H\end{matrix}$, separated. This formed long, hexagonal crystals, m. p. 254°, and yielded phthalophenone and the amino-acid on hydrolysis.

α-Phthalimino-α-methylbutyric acid was also converted into the *chloride*, but this could neither be solidified nor distilled. It was condensed with benzene at 100°, and again it was found that the resinous product consisted of a small amount of the expected *α-phthalimino-α-methylbutyrophenone*, $C_8H_4O_2{:}N\cdot CMeEt\cdot COPh$, which formed long, hexagonal plates, m. p. 78—80°, mixed with an amount of *1 : 1-diphenylphthalimidyl-α-methylbutyric acid*, $C_{25}H_{23}O_3N$, rhombic columns, m. p. 283°, which increased with the duration and temperature of the reaction. They were separated by reason of the solubility of the latter in hot ammonia solutions and insolubility in ether. The former gave the *hydrochloride* of *α-amino-α-methylbutyrophenone*, $COPh\cdot CMeEt\cdot NH_2,HCl$ (*picrate*, m. p. 193°), and the latter phthalophenone and the amino-acid, on hydrolysis.

It was found that both acyl chlorides decomposed on distillation. The α-phthalimino-α-ethylbutyryl chloride yielded thereby *γ-phthalimino-Δ$^{\beta}$-pentene*, $C_8H_4O_2{:}N\cdot CEt{:}CHMe$, which was purified by distillation in steam and obtained in fatty scales, m. p. 83°, with a stupefying odour. It yielded phthalimide and diethyl ketone when boiled with hydriodic acid. The α-methyl derivative yielded the very similar *β-phthaliminobutene*, $C_8H_4O_2{:}N\cdot CMe{:}CHMe$ or $C_8H_4O_2{:}N\cdot CEt{:}CH_2$, m. p. 90°, b. p. 215°/16 mm. Both substances absorbed bromine readily, and a crystalline *dibromide*, leaflets, m. p. 77—78°, was prepared from the latter. This lost hydrogen bromide in a vacuum at 100° and gave two *products*, one of which, m. p. 92—93°, had the composition of α-phthaliminobromobutene. J. C. W.

Resolution of Phenylglyceric Acid of M. p. 141° into its Optically Active Components. C. N. Riiber (*Ber.*, 1915, **48**, 823—831).—Two isomeric phenylglyceric acids have been synthesised, one, m. p. 141°, by oxidation of ordinary cinnamic acid, and the other, m. p. 121°, by oxidation of *allo*cinnamic acid. The latter acid has been resolved (Plöchl and Mayer, A., 1897, i, 528), but the former has hitherto

resisted attempts to separate it into enantiomorphous components. The less fusible acid has now been successfully resolved by recrystallisation of its morphine salt from acetone.

The necessary phenylglyceric acid was prepared by oxidation of methyl cinnamate in alcoholic solution by potassium permanganate, and hydrolysing the product. On resolution it yielded a less soluble morphine salt of an active acid, $[\alpha]_D^{20}$ −39·63°, $[\alpha]_C^{20}$ −31·42°, $[\alpha]_E^{20}$ −50·90° in water, $[\alpha]_D^{20}$ −30·48° in alcohol, $[\alpha]_D^{20}$ −36·43° in acetone. The more soluble morphine salt gave an acid of $[\alpha]_D^{20}$ +39·57° (in water). Both acids crystallise in tablets, m. p. 164° (monoclinic system,

$$a : b : c = 2{\cdot}1875 : 1 : 2{\cdot}0794 ; \ \beta = 93{\cdot}88°),$$

and dissolve in water at 20° to the extent of 4·10 grams per 100 grams, whereas the racemic acid dissolves to the extent of 9·00 grams. Physico-chemical examination proved the inactive synthetic acid to be a racemic mixture and not a compound.

The higher optical activity of these acids compared with those derived from the racemic acid, m. p. 121°, is in accord with the relative structures expected for the oxidation products of a *trans*- and a *cis*-acid respectively. D. F. T.

Condensation of Ethyl 1 : 3-Dihydroxy-2-naphthoate with Benzaldehyde. H. Nowak (*Monatsh.*, 1914, **35**, 909—924).—Ethyl 1 : 3-dihydroxy-2-naphthoate readily condenses with benzaldehyde in the presence of hydrogen chloride and hydrogen bromide, yielding the compounds (X = Cl or Br): $C_6H_4<\begin{matrix}C(CHPhX):C\cdot OH\\ C(OH)=\!=\!=C\cdot CO_2Et\end{matrix}$ or $C_6H_4<\begin{matrix}CH(CHPhX)\cdot CO\\ C(OH)=\!=\!=C\cdot CO_2Et\end{matrix}$, in which the halogen atoms are even more reactive than in the corresponding monohydroxy-derivatives (Friedel, A., 1910, i, 741 ; compare also A., 1913, i, 1345).

Ethyl 2 : 4-*dihydroxy*-1-α-*chlorobenzyl*-3-*naphthoate*, prepared by passing hydrogen chloride into a well-cooled mixture of the ester and benzaldehyde in equimolecular proportions, crystallises in pale yellow needles or microscopic plates, m. p. 125°, decomposes slowly when kept, and gives a scarlet-red coloration with sulphuric acid ; if two molecules of ethyl 1 : 3-dihydroxy-2-naphthoate are employed, *phenyldi*-2 : 4-*dihydroxy*-3-*carbethoxy*-α-*naphthylmethane* [*ethyl benzylidenebis*-2 : 4-*dihydroxynaphthalene*-3-*carboxylate*], $CHPh[C_{10}H_4(OH)_2\cdot CO_2Et]_2$, m. p. 198° (decomp.), is produced.

Ethyl 2 : 4-*dihydroxy*-1-α-*bromobenzyl*-3-*naphthoate* crystallises in yellow needles, m. p. 132°.

Both the chloro- and bromo-derivatives react instantly with water in acetone solution, yielding *ethyl* αα′-*oxidobis*-1-*benzyl*-2 : 4-*dihydroxynaphthalene*-3-*carboxylate*, $O[CHPh\cdot C_{10}H_4(OH)_2\cdot CO_2Et]_2$, crystallising in glistening, yellow, microscopic needles, m. p. 191°, and with acetic anhydride in the presence of anhydrous sodium acetate to form *ethyl* 2 : 4-*diacetoxy*-1-α-*acetoxybenzyl*-3-*naphthoate*,

$$OAc\cdot CHPh\cdot C_{10}H_4(OAc)_2\cdot CO_2Et.$$

Ethyl 2 : 4-*dihydroxy*-1-α-*methoxybenzyl*-3-*naphthoate*.

$$OMe\cdot CHPh\cdot C_{10}H_4(OMe)_2\cdot CO_2Et,$$

prepared by boiling the chloro-compound in methyl-alcoholic solution, crystallises in yellow needles, m. p. 151°; the corresponding *ethoxy*-derivative has m. p. 204°. The chloro-compound reacts with ammonia in benzene solution, yielding *ethyl aa'-iminobis*-2 : 4-*dihydroxy*-1-*benzyl*-3-*naphthoate*, $NH[CHPh\cdot C_{10}H_4(OH)_2\cdot CO_2Et]_2$, crystallising in felted needles, m. p. 156°; with aniline it yields *ethyl* 2 : 4-*dihydroxy*-1-*α-anilinobenzyl*-3-*naphthoate*, $NHPh\cdot CHPh\cdot C_{10}H_4(OH)_2\cdot CO_2Et$, m. p. 149°.

Ethyl 2 : 4-*dihydroxy*-1-*benzyl*-3-*naphthoate*,

$$CH_2Ph\cdot C_{10}H_4(OH)_2\cdot CO_2Et,$$

prepared by heating the chloro-compound with hydriodic acid and red phosphorus in acetic anhydride solution, forms yellow crystals, m. p. 107°, gives a red coloration with sulphuric acid, and resembles the above-mentioned methoxy-, ethoxy-, and anilino-derivatives in being reconverted into the original chloro-compound by the action of hydrogen chloride in ethereal solution. F. B.

The Condensation of Terephthalaldehyde with Methyl 2-Hydroxy-3-naphthoate. KARL LUGNER (*Monatsh.*, 1915, **36**, 143—167).—An extension of the earlier researches on the behaviour of methyl and ethyl 2-hydroxy-3-naphthoates towards various aldehydes (Friedl, A., 1910, i, 741; Rebek, A., 1913, i, 1346; Weishut, A., 1913, i, 1347; Seib, A., 1913, i, 1348).

In the presence of hydrogen chloride, terephthalaldehyde slowly reacts with an ethereal suspension of methyl 2-hydroxy-3-naphthoate, giving *methyl* 2-*hydroxy*-1-*α-chloro*-p-*aldehydobenzyl*-3-*naphthoate*,

$$C_6H_4\begin{<}\begin{matrix}C(CHCl\cdot C_6H_4\cdot CHO)\\ CH\!=\!=\!=\!=C(CO_2Me)\end{matrix}\end{>}C\cdot OH,$$

yellow needles, m. p. 180·5°. It was not found possible to cause the second aldehyde group to enter into the reaction. The substance gives a red coloration with sulphuric acid, and a green one with ferric chloride. If hydrogen bromide is used in place of the chloride for the condensation reaction, the product is *methyl* 2-*hydroxy*-1-*α-bromo*-p-*aldehydobenzyl*-3-*naphthoate*, a yellow, crystalline solid, m. p. 169—170°, which gives a bluish-violet coloration with sulphuric acid and a green with ferric chloride. Both the bromo- and the chloro-compounds are readily decomposed by water in acetone solution, giving the corresponding *methyl* 2-*hydroxy*-1-*α-hydroxy*-p-*aldehydobenzyl*-3-*naphthoate*,

$$C_6H_4\begin{<}\begin{matrix}C[CH(OH)\cdot C_6H_4\cdot COH]\\ CH\!=\!=\!=\!=C(CO_2Me)\end{matrix}\end{>}C\cdot OH,$$

yellow, microscopic prisms, m. p. 167° (*thiosemicarbazone*, microscopic needles, m. p. 210°, forms an amorphous *silver* salt), which gives similar colour reactions to the chloro-compound. The velocity of the reaction with water is less than that shown by the analogous benzaldehyde condensation products, and as might be expected the hydrolysis of the bromo-compound proceeds much more rapidly than that of the chloro-compound. When boiled with an approximately quinquemolecular proportion of methyl alcohol in ethereal solution, the chloro-compound is converted into *methyl* 2-*hydroxy*-1-*α-methoxy*-p-*dimethoxymethylbenzyl*-3-*naphthoate*,

$$C_6H_4\begin{<}\begin{matrix}C[CH(OMe)\cdot C_6H_4\cdot CH(OMe)_2]\\ CH\!=\!=\!=\!=\!=\!=\!=C(CO_2Me)\end{matrix}\end{>}C\cdot OH,$$

yellow needles, m. p. 150°, both the chloro- and the aldehyde groups having entered into reaction; this substance gives colorations with sulphuric acid and ferric chloride similar to those given by the chloro-compound. In benzene solution equimolecular quantities of phenol and the chloro-condensation product react with the calculated amount of sodium, yielding very pale yellow needles of *methyl* 2-*hydroxy*-1-α-*phenoxy*-p-*aldehydobenzyl*-3-*naphthoate*,

$$C_6H_4\begin{<}\begin{matrix}C[CH(OPh)\cdot C_6H_4\cdot CHO]\\ CH\!=\!\!=\!\!=\!

solution, the product being *ω-benzeneazophenylamino-ω-2-hydroxy-3-carbomethoxy-α-naphthyl-p-tolualdehydebenzeneazophenylanil*

$$C_6H_4<\begin{matrix}C[CH(NH\cdot C_6H_4\cdot N_2Ph)\cdot C_6H_4\cdot CH{:}N\cdot C_6H_4\cdot N_2Ph]\\ CH\!=\!\!=\!\!=\!

which, when boiled with water, is converted into the yellow anhydrous phthalein. The *dibenzoate*, m. p. 284—285°, crystallises in white needles. *Tetrabromo-γ-orcinolphthalein diacetate*, m. p. 282—283°, crystallises in white, rhombohedral plates. γ-Orcinolphthalein yields an orange-coloured, unstable *diammonium* salt, whilst the tetrabromo-derivative combines with 4 mols. of ammonia to form a dark-red, unstable *salt*. The phthalein unites with 1 mol. of hydrogen chloride to form a yellow *hydrochloride*.

The orcinoltetrachlorophthaleins were prepared by fusing orcinol with tetrachlorophthalic acid in presence of zinc chloride, and their separation was effected by similar means to those employed in the case of the orcinolphthaleins.

α-Orcinoltetrachlorophthalein, $C_{22}H_{12}O_5Cl_4$, is colourless when pure and dissolves in alkali hydroxide to form solutions of a pure blue colour; the *diacetate*, m. p. 292°, forms minute, colourless, rhombic crystals.

β-Orcinoltetrachlorophthalein is also colourless when pure. It is decomposed by hot potassium hydroxide solution with elimination of chlorine and formation of a dark red substance. A white *hydrate* is obtained when a solution of the phthalein in alkali hydroxide is acidified. The *diacetate*, m. p. 239°, forms white crystals.

γ-Orcinoltetrachlorophthalein crystallises in white, slender needles; its *diacetate*, m. p. 252—253°, forms long, flat needles.

The absorption spectra of the orcinolphthaleins, tetrabromo-orcinolphthaleins, orcinoltetrachlorophthaleins, and tetrabromo-γ-orcinoltetrachlorophthalein have been investigated and the transmission curves plotted. The curves for the γ-phthaleins are those typical of fluorescent substances, indicating that these compounds are derivatives of fluorescein and therefore have a similar structure.

The constitutions of the orcinolphthaleins and their derivatives are discussed. E. G.

Chromoisomeric Salts of Phenolic and Enolic Derivatives Similar to Ethyl Acetoacetate. A. Hantzsch (*Ber.*, 1915, **48**, 785—797).—The author has been able to produce chromoisomeric salts with simpler compounds than those used hitherto, namely, with nitrogen-free compounds analogous to ethyl acetoacetate. Chromoisomerism cannot be obtained with symmetrical compounds of the structure $COR{\cdot}CH_2{\cdot}COR$, as has already been demonstrated with indandione derivatives (Hantzsch, A., 1912, i, 869), but with unsymmetrical compounds of the ethyl acetoacetate type the existence of two series of coloured salts may be expected because of the two possible structures $OM{\cdot}CR{:}CH{\cdot}COR'$ and $COR{\cdot}CH{:}CR'{\cdot}OM$ (where M represents the metal) for the enolic salt; the anions of these pairs of chromoisomeric salts will be identical, except for the position of the valency by which the metal atom was attached. As has been shown earlier, the salts will probably undergo further structural adjustment (Hantzsch, A., 1910, i, 812; Hantzsch and Voigt, A., 1912, i, 151), producing "conjugated" enolic salts of the type $\overset{\text{OM}\cdots\cdots\text{O}}{\overset{|}{\text{CR}}{:}\text{CH}{\cdot}\overset{||}{\text{CR}'}}$ and $\overset{\text{O}\cdots\cdots\text{MO}}{\overset{||}{\text{CR}}{\cdot}\text{CH}{:}\overset{|}{\text{CR}'}}$, where M represents the metal. On account of the

likelihood of a condition of equilibrium between the two possible chromoisomeric salts in a solution, spectroscopic examination in the ultraviolet region is not possible, and the investigation must be limited to examples showing absorption in the visible spectrum. For this reason ethyl acetoacetate itself could not be applied to the investigation, and use was made of ethyl succinylsuccinate, ethyl 2 : 5-dihydroxyterephthalate, and ethyl dihydroxybenzoquinonedicarboxylate. These esters can give two classes of salts represented by the structures $OM\cdot C{:}C\cdot CO_2R$ and $CO\cdot C{:}C(OR)\cdot OM$, which may be distinguished by the respective terms "enol" and "ethoxyenol" salts, but the author prefers a general extension of the two terms "benzenoid" or "phenolic" salts to the former class, and "quinonoid" or "enolic" salts to the latter, although these terms are more intimately associated with the salts of ethyl dihydroxyterephthalate. Ethyl dihydroxyterephthalate exists in two chromoisomeric forms, which are colourless and yellow respectively; the colourless form is optically identical with ethyl dimethoxyterephthalate, $C_6H_2(OMe)_2(CO_2Et)_2$, and must therefore be the true dihydroxy-ester, whilst the yellow variety must be the quinonoid enol ester. From analogy the conclusion is drawn that of the above chromoisomeric metallic salts the less strongly coloured isomeride possesses the "benzenoid phenolic" structure, and this view receives strong confirmation by the colourless ethyl dihydroxyterephthalate giving yellow salts, whilst the yellow enolic isomeride forms red salts.

On account of the presence of two chromophoric groups in the esters named above, there is a possibility of three chromoisomeric forms of each salt, namely, of dibenzenoid, diquinonoid, and of benzenoid-quinonoid structure respectively. In the case of ethyl dihydroxybenzoquinonedicarboxylate three forms can actually be observed, yellow, orange, and red respectively, but generally only the yellow and red varieties have been obtained.

It is not always possible to isolate two differently coloured forms of the same salt, and as additional criteria of chromoisomerism are held the occurrence of a difference in colour between any two salts with different alkali or alkaline-earth metals, a difference in colour between the compound and its alcoholate or hydrate, or between the two latter derivatives, and, finally, a difference in colour between the compound and its aqueous or alcoholic solution.

[With R. H. Clark and R. Andrich.]—Ethyl succinylsuccinate gives colourless mono-metallic salts with all alkali metals, aqueous and alcoholic solutions, however, being deep yellow; the *dilithium* salt was red, but gave a yellow dihydrate; *barium* salt, yellow, giving a red dihydrate; *calcium* salt, yellow, both when anhydrous and as dihydrate; *magnesium* salt, yellow, giving a red dihydrate (compare Herrmann, A., 1882, 712).

The following salts were prepared from ethyl 2 : 5-dihydroxyterephthalate; *lithium* salt, yellow, giving a red alcoholate; *barium* salt yellow, giving a red dihydrate; *calcium* salt, red; *magnesium* salt, yellow, giving a red dihydrate. All salts of dihydroxyterephthalic acid with metals which yield colourless ions are colourless, any yellow or brown coloration which may be observable being due to oxidation.

[With V. EYRE.]—Ethyl dihydroxybenzoquinonedicarboxylate was converted into the following salts: *diammonium* salt, *dimethylammonium* salt and *methylammonium* salt, yellow; *trimethylammonium* salt, yellow, giving a red compound with $1C_6H_6$, and also an unstable orange compound with $1CHCl_3$; *dipyridine* salt, red; *monopyridine* salt, yellow; *tetramethylammonium* salt, yellow or red, the two varieties being inter-convertible and giving identical solutions.

D. F. T.

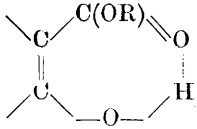
The Chromoisomerism of Derivatives of 2 : 5-Dihydroxyterephthalic Acid as Phenol–Enol Isomerism. A. HANTZSCH (*Ber.*, 1915, **48**, 797—816).—It has been known for a considerable time (Herrmann, A., 1882, 712) that the esters of dihydroxyterephthalic acid can exist in two forms, one colourless and labile, the other yellowish-green and stable, and that the esters of the corresponding dihalogen-dihydroxyterephthalic acids, $C_6X_2(OH)_2(CO_2H)_2$, exhibit similar behaviour (Hantzsch and Zeckendorf, A., 1888, 278; Hantzsch, A., 1906, i, 858). This isomerism is not of the simple keto-enol type, nor is it merely a case of polymorphism as suggested by Nef (A., 1890, 983), but it is due to the existence of the esters in two different constitutions, namely, a colourless benzenoid form and a greenish-yellow quinonoid form with the characteristic groupings $OR\cdot CO\cdot \overset{|}{C}:\overset{|}{C}\cdot OH$ and $OR\cdot C(OH):\overset{|}{C}\cdot \overset{|}{C}O$ respectively (compare Hantzsch, preceding abstract), and of the free acid in the corresponding stuctures $OH\cdot CO\cdot \overset{|}{C}:\overset{|}{C}\cdot OH$ and $C(OH)_2:\overset{|}{C}\cdot \overset{|}{C}O$. This view is based on the existence of two distinct forms of methyl dichlorodihydroxyterephthalate, which are both remarkably stable, and by its formation of colourless or yellow solutions according to the medium, the two classes of solutions corresponding with the two forms of the ester. In the case of other derivatives such as the ethyl ester of the dichlorodihydroxyterephthalic acid, the esters of the corresponding dibromo- and di-iodo-acids, and dichlorodihydroxyterephthalic acid itself, only the colourless form is stable, whilst with dihydroxyterephthalic acid and its esters the yellow form is stable. In solution an equilibrium is generally attained in which the percentage of the yellow quinonoid or enol form increases as one passes along the series of solvents, dilute hydrochloric acid, water, methyl alcohol, ethyl alcohol, amyl alcohol, ether, chloroform, tetrachloromethane, benzene; with the exception of dihydroxyterephthalic acid and its esters, in which the yellow form has the greater stability throughout, a solution in water contains the solute mainly in the colourless form, whilst in benzene solution the solute is almost entirely of the yellow modification.

The absorption spectra of the yellow and colourless solutions are strikingly similar, so that the forms are in all probability both monomolecular; the considerable influence of the nature of the solvent and of the temperature on the absorption is not observed with compounds such as diacyl derivatives of the type $C_6Cl_2(OAc)_2(CO_2R)_2$, in which the phenolic hydrogen has been replaced by less mobile radicles, so that it is natural to refer the equilibrium to an intramolecular change in which these hydrogen atoms are involved. The respective constitutions $OR\cdot CO\cdot \overset{|}{C}:\overset{|}{C}\cdot OH$ and $OR\cdot C(OH):\overset{|}{C}\cdot \overset{|}{C}O$ are applied to the

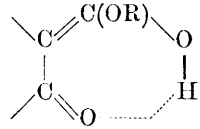
colourless and yellow modifications, because the colourless solutions of the esters of dichlorodihydroxyterephthalic acid are optically almost identical with those of the corresponding dimethoxy-ester,

$$C_6Cl_2(OMe)_2(CO_2R)_2,$$

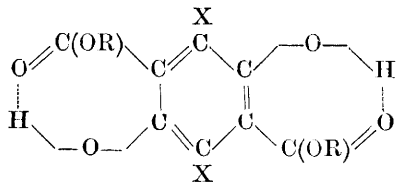
whilst the yellow modifications are able to form salts, and so must still contain a hydroxyl group. By the existence of subsidiary valencies, however, these two constitutions may undergo slight modification into



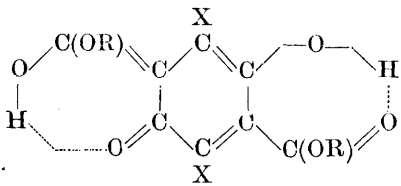
and



in which case the phenomenon becomes one of "allodesmy," the only difference between the substances then lying in the position of the valencies. It is believed that in the yellow forms of the compounds under discussion only one of the hydroxyl groups has undergone conversion into the quinonoid structure, so that the colourless benzenoid or diphenolic compound is representable by the formula I, whilst the structure of the monoquinonoid or phenolic-enolic compound is represented by formula II.



(I.)



(II.)

Methyl dichlorodihydroxyterephthalate is distinguished from the other esters of this acid by the relative stability of its yellow modification, the colourless ester melting at 177° to a yellow liquid which gives the yellow modification on cooling, whilst the inverse change from yellow to colourless occurs near 140°. Separation from solution generally yields the ester as a mixture of the two modifications. With the ethyl ester the relative stability of the colourless form is so great that the solid obtained from a benzene solution has only a fleeting yellow colour. With methyl and ethyl dibromodihydroxyterephthalates the yellow modification is again very unstable.

Ethyl dichlorodimethoxyterephthalate, $C_6Cl_2(OMe)_2(CO_2Et)_2$, prepared by heating the yellow potassium salt of ethyl dichlorodihydroxyterephthalate with methyl iodide or methyl sulphate, forms colourless needles, m. p. 177°.

Methyl dibromodihydroxyterephthalate, $C_6Br_2(OH)_2(CO_2Me)_2$, melts at 205° to a yellow liquid, but again becomes colourless on re-solidifying; *methyl di-iododihydroxyterephthalate* decomposes at 188°.

Ethyl dimethoxyterephthalate (Nef, *loc. cit.*) in solution exists almost entirely as the yellow enol ester, whereas by sublimation the yellow form can be converted into the labile phenolic form.

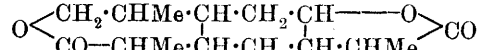
Dihydroxyterephthalic acid exists as a colourless dihydrate of the

phenolic structure, the yellow anhydrous acid being of enolic structure, whilst with dichlorodihydroxyterephthalic acid the anhydrous acid is colourless and of phenolic structure, the dihydrate being yellow and of enolic structure. As dihydroxyterephthalic acid and its esters give solutions of approximately the same yellow colour, the dissolved substances are believed to be present almost entirely as the yellow enolic forms, or in other words as pseudo-derivatives.

Absorption curves are given for solutions of many of the compounds mentioned. It is noted that contrary to the views of Kauffmann, the methoxyl and hydroxyl groups are of approximately equal auxochromic effect, and that any decided difference between the colour and absorption of a hydroxyl compound and the corresponding methoxyl derivative must be attributed to intramolecular constitutive change. Accordingly, the yellow dihydroxypyromellitic acid and the colourless dimethoxypyromellitic acid (Nef, *loc. cit.*) cannot be structurally identical, and the difference in colour is to be attributed to the existence of two chromoisomerides. D. F. T.

Santonin. XII. α-Tetrahydrosantonilide. E. Wedekind (*Ber.*, 1914, **47**, 2483—2485).—α-Tetrahydrosantonin has already been submitted to oxidation by chromic acid (Wedekind and Beniers, A., 1913, i, 476), but the process is not always satisfactory, and Caro's acid has now been applied with a gratifying result.

When a chloroform solution of α-tetrahydrosantonin is gradually introduced with stirring into a mixture of ammonium persulphate and somewhat diluted sulphuric acid, there is produced a lactone which from its analogy to campholide is termed *α-tetrahydrosantonilide.* This substance, for which the formula

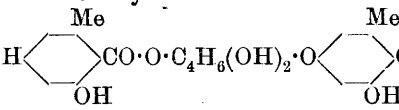


is proposed, is a crystalline solid, m. p. 159·5°, $[\alpha]_D$ −47·15° (in benzene), −31·2° (in chloroform), −35·1° (in ethyl alcohol).

D. F. T.

Synthesis of Two α-Hydroxy*iso*camphoronic Acid Lactones, and their Relation to Dehydrocamphenic Acid. P. Lipp (*Ber.*, 1914, **47**, 2994—2997).—Kachler (A., 1878, 513) obtained a compound, $C_9H_{12}O_6$, m. p. 226°, by heating *iso*camphoronic acid with bromine, which was most probably a mixture of the isomeric lactonic acids which Aschan prepared by the action of nitric acid on dehydrocamphenic acid (A., 1910, i, 710), although Tiemann and Semmler regarded it as "*iso*camphorenic acid" (A., 1895, i, 478). The author finds that when equimolecular proportions of *iso*camphoronic acid and bromine are heated at 120—130° for four hours the product is, indeed, the *cis*-lactonic acid, $C_9H_{12}O_6,H_2O$, m. p. of the anhydrous acid, 185—186·5° (corr.), whereas the product after eight hours' heating is the *trans*-form, m. p. 256°. The formula which the author proposed for these α-hydroxy*iso*camphoronic acid lactones, $\begin{matrix}CMe_2\cdot CH\cdot CH_2\cdot CO_2H\\ |\\ CO\cdot O\cdot CH\cdot CO_2H\end{matrix}$ (A., 1914, i, 542), has been supported by Hintikka (A., 1914, i, 973).

*iso*Camphoronic acid can scarcely be an intermediate product of the oxidation of dehydrocamphenic acid to these lactones by nitric acid, for it is not attacked at all by that agent. J. C. W.

Structure of Erythrin. ERNST ZERNER (*Monatsh.*, 1914, **35**, 1021—1024).—The author advances arguments against Luynes's (*Annalen*, 1864, **132**, 355) and Hesse's (A., 1898, i, 532) formulæ for erythrin and shows that the behaviour of the compound is best represented on the assumption that the orsellinic acid residues are differently attached to the erythritol molecule as shown in the following formula:  . This formula not only explains the acid character of erythrin, but also accounts for the fact that only one molecule of orsellinic acid is removed by hydrolysis. The picroerythrin resulting from the hydrolysis still possesses acid properties, gives a violet coloration with ferric chloride, and, therefore, must contain a free hydroxyl in the ortho-position to the carboxyl group. F. B.

δδ-Diphenylsemicarbazide as a Reagent for the Detection of Carbonyl Derivatives. B. TOSCHI and A. ANGIOLANI (*Gazzetta*, 1915, **45**, i, 205—213).—δδ-Diphenylsemicarbazide (A., 1914, i, 740) forms an excellent reagent for the detection of carbonylic compounds and in many cases gives better results than semicarbazide itself. It is highly stable towards light and air, whereas semicarbazide tends to decompose into hydrazocarbonamide and hydrazine (compare Curtius and Heidenreich, A., 1896, i, 143). Further, the δδ-diphenylsemicarbazones separate more readily, and are appreciably less soluble and more easily purified, than the corresponding semicarbazones.

The δδ-diphenylsemicarbazones of aliphatic carbonyl compounds are prepared by adding to an aqueous solution of the hydrochloride of the base the calculated quantity of an aqueous or aqueous-alcoholic solution of the aldehyde or ketone and then sodium acetate. These diphenylsemicarbazones are sparingly soluble in water and are somewhat basic in character, dissolving in the cold in dilute acids, by which they are decomposed, with regeneration of the aldehyde or ketone, on heating. Of special interest in practice are the compounds given by the sugars, and these are being investigated.

The δδ-diphenylsemicarbazones of aromatic aldehydes are obtained by adding an alcoholic solution of the aldehyde (1 mol.) to an alcoholic solution of the base (1 mol.). They separate immediately as crystalline precipitates, are usually very sparingly soluble in alcohol, are readily hydrolysed by boiling dilute acids, and dissolve in concentrated sulphuric acid with characteristic colorations.

δδ-Diphenylsemicarbazones of the following compounds have been prepared. *Acetone*, $CMe_2{:}N{\cdot}NH{\cdot}CO{\cdot}NPh_2$, colourless needles, m. p. 119°. *Acetaldehyde*, $C_{15}H_{15}ON_3$, long, silky needles, m. p. 153°. *Heptaldehyde*, $C_{21}H_{27}ON_3$, colourless needles, m. p. 133—134°. *Ethyl acetoacetate*, $CO_2Et{\cdot}CH_2{\cdot}CMe{:}N{\cdot}NH{\cdot}CO{\cdot}NPh_2$, white crystals, m. p.

103—104°. *Dextrose*, $C_6H_{12}O_5{:}N{\cdot}NH{\cdot}CO{\cdot}NPh_2,H_2O$, white needles, m. p. 164—166°. *Cinnamaldehyde*, $CHPh{:}CH{\cdot}CH{:}N{\cdot}NH{\cdot}CO{\cdot}NPh_2$, yellow needles, m. p. 164—166°, giving an orange-red coloration with concentrated sulphuric acid in the cold. *Cuminaldehyde*, $C_{22}H_{23}ON_3$, white crystals, m. p. 162°, giving a greenish-yellow coloration with concentrated sulphuric acid in the cold. *Salicylaldehyde*, $C_{20}H_{17}O_2N_3$, colourless needles, m. p. 209°, giving a yellow coloration with cold concentrated sulphuric acid. *Vanillin*, $C_{21}H_{19}O_3N_3$, white needles, m. p. 180—181°, giving a yellow coloration with cold concentrated sulphuric acid. *Piperonaldehyde*, $C_{21}H_{17}O_3N_3$, yellow needles, m. p. 173°, giving an orange-red coloration with concentrated sulphuric acid in the cold. *Benzophenone*, $C_{26}H_{21}ON_3$, white needles, m. p. 186—187°. *Citronellaldehyde*, $C_{23}H_{29}ON_3$, white crystals, m. p. 109—110°. *Camphor*, $C_{23}H_{27}ON_3$, silky needles, m. p. 154—155°. T. H. P.

Action of Nitroso-derivatives on Unsaturated Compounds. Luigi Alessandri (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 62—67).—The action of nitrosobenzene on safrole probably yields first the intermediate compound, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH(NPh{\cdot}OH){\cdot}CH{:}NPh{:}O$, which subsequently loses phenylhydroxylamine, giving the compound $CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{:}NPh{:}O$ (compare Angeli, Alessandri and Pegna, A., 1910, i, 552). The phenylhydroxylamine liberated would then react with the nitrosobenzene with formation of azoxybenzene, which is, indeed, obtained in considerable quantity. That this view of the reaction is correct is supported by the fact that the yield of the crude phenylated oxime is increased from 20% to 40% when the proportion of nitrosobenzene taken is increased from 1 mol. to 3 mols. per mol. of safrole.

The action of nitrosobenzene (3 mols.) on estragole, myristicin and methyleugenol (1 mol.) yields yellow compounds, m. p. 165°, 180°, and 154° respectively, which are rapidly decomposed by the action of sunlight.

The action of nitrosobenzene on parsley-apiole follows a somewhat different course, the products being: (1) *apioleacraldehyde*, $CHO{\cdot}CH{:}CH{\cdot}C_6H(OMe)_2{:}CH_2O_2$(?), yellow crystals, m. p. 137°, which forms an *oxime*, m. p. 172°, and (2) apiolaldehyde (?), m. p. about 100°.

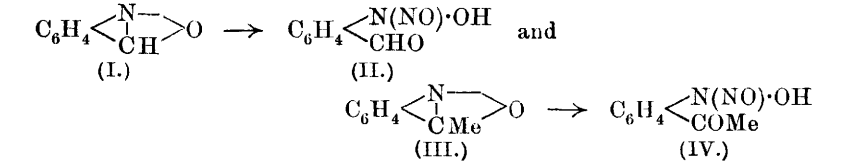
Asarone and nitrosobenzene yield asarylaldehyde, azoxybenzene and the *N-phenyl* derivative of *asarylaldoxime*, $O{:}NPh{:}CH{\cdot}C_6H_2(OMe)_3$, which forms yellow crystals, m. p. 125°, and gives asarylaldehyde when hydrolysed by means of dilute acid.

When added to caoutchouc which has been allowed to swell in a small volume of benzene, nitrosobenzene dissolves with formation of a characteristic emerald-green coloration and marked cooling. The colour of the mixture afterwards changes successively to bottle-green, brownish-green and brownish-red, and part of the product formed remains undissolved as a reddish-yellow, gelatinous mass. When treated with light petroleum, both the solution and the gelatinous substance yield an ochre-yellow, amorphous compound, which gives analytical results corresponding with the formula $C_{58}H_{61}O_9N_5$, and

softens at 135—140°, afterwards undergoing energetic decomposition. When this compound is washed with carbon disulphide and repeatedly boiled with ether, the percentage of oxygen present increases from about 15 to about 19. The compound is not very sensitive to the action of light, but when treated with potassium permanganate it gives nitrosobenzene and an odour resembling that of carbylamines.

T. H. P.

Anthranil. XX. Anthranil and Methylanthranil. Eug. Bamberger (*Ber.*, 1915, **48**, 537—582).—In a long series of papers (chiefly 1909 and 1910) Bamberger and others have shown that anthranil (I) is homologous with methylanthranil, which was proved to have the formula III (A., 1903, i, 560). Part of the evidence was to the effect that the compounds both form phenylnitrosohydroxylamines when treated with nitrous acid, thus:



(I.) (II.) (III.) (IV.)

These compounds were also proved to be homologous, by reduction to diazonium salts.

The derivative of anthranil, namely, *o*-aldehydophenylnitrosohydroxylamine (II), was easily isolated in the crystalline state (A., 1909, i, 509), but the derivative of methylanthranil, namely, *o*-acetylphenylnitrosohydroxylamine (IV), could only be characterised by colour reactions (*ibid.*). As the nitrosation was carried out in the presence of hydrochloric acid, which chlorinates much of the methylanthranil, the reaction has now been studied in the presence of sulphuric acid. It has been found, however, that the reaction follows a new course.

The chief product is easily reduced to a diazonium salt, is a ketone, reacts vigorously with diazomethane, and undergoes rearrangement when warmed with dilute acids into two compounds which are recognised as nitroanilines, namely, 3-nitro-2-aminoacetophenone and 5-nitro-2-aminoacetophenone, $NO_2 \cdot C_6H_3Ac \cdot NH_2$. It is, therefore, *o*-acetylphenylnitroamine [*o*-nitroaminoacetophenone], $C_6H_4Ac \cdot NH \cdot NO_2$.

This discovery throws some light on the constitution of an acidic by-product, which was obtained in very small quantity in the case of anthranil, as a substance which accompanies the *o*-nitrosobenzaldehyde obtained by decomposing crude *o*-aldehydophenylnitrosohydroxylamine (A., 1911, i, 60), for it is in reality the homologue of the above nitroamine, namely, *o*-nitroaminobenzaldehyde,

$$CHO \cdot C_6H_4 \cdot NH \cdot NO_2.$$

The net result of the action of nitrous acid is, therefore, this; anthranil yields much of the nitrosohydroxylamine and very little of the isomeric nitroamine, whilst methylanthranil gives extremely little of the former and a fair amount of the latter. The reaction is merely the addition of nitrous acid to the opened benzo*iso*oxazole ring, CHO(or Ac)·C_6H_4·N= and is explained in two or three ways.

Action of sodium nitrite and sulphuric acid on methylanthranil.—The preparation of *o*-nitroaminoacetophenone, free from the by-products of the reaction, is a matter of considerable difficulty. Two grams of methylanthranil were quickly stirred into an emulsion with 40 grams of about 15% sulphuric acid in a tall beaker, and then a solution of 1·33 grams of sodium nitrite in 2·3 c.c. of water was added during forty minutes at the rate of 3 drops per minute. The liquid was cooled by ice, vigorously stirred, and the nitrous fumes were removed by a brisk current of air playing over the surface. When no more nitrous acid could be detected, the solution was saturated with ammonium sulphate and extracted with ether. The aqueous extract contained *o*-acetylbenzenediazonium sulphate, for the azo-dye with *β*-naphthol, m. p. 198·5—199° (A., 1903, i, 560), was obtained from it. The ethereal layer was shaken with dilute ammonia. The residual ether contained a trace of a feebly acid substance removable by sodium hydroxide, and also much unchanged methylanthranil (purified by the mercuric chloride compound) and some acetophenone (identified as the phenylhydrazone). The ammoniacal extract was exposed to a draught and concentrated to a small bulk, cooled with ice, and then carefully treated with 2*N*-sulphuric acid until the precipitate no longer redissolved, and finally with 0·5*N*-sulphuric acid. The precipitated nitroamine was filtered and washed with cold water. Other by-products included a crystalline base, a neutral, coloured substance, and an acid with indicator properties.

o-*Nitroaminoacetophenone*, $C_6H_4Ac\cdot NH\cdot NO_2$, crystallises in colourless, silky needles from cold water or sparkling prisms from carbon tetrachloride, m. p. 103—104°. It is quite stable in the dark, and may be distilled in steam without much decomposition. It is acid to litmus, methyl-orange and Congo-red, but not to tropæolin. It does not reduce ammoniacal silver nitrate, gives a deep reddish-violet colour when a trace of zinc is added to a mixture with an acetic acid solution of *α*-naphthylamine, and is reduced by nitrous acid to the diazonium salt (*β*-naphthol dye) which yields *o*-hydroxyacetophenone on boiling. It forms a *silver* salt, white needles, *copper* salt, very long, silky needles, *lead* salt, silky needles, and a soluble barium salt. The *phenylhydrazone*, $C_{14}H_{14}O_2N_4$, forms golden-yellow, brilliant leaflets, m. p. 132·5°, which dissolve in weak alkalis without colour and in concentrated sulphuric or hydrochloric acid with deep blue colours. The p-*nitrophenylhydrazone*, $C_{14}H_{13}O_4N_5$, forms brownish-yellow or dark golden-yellow, glistening needles, m. p. 173°. The powder dissolves in 2*N*-sodium hydroxide with dark blood-red colour, a delicate reaction for *o*-nitroaminoacetophenone, but when covered with 2*N*-sodium carbonate it dissolves slightly to form a yellow solution, which soon deposits bronze-coloured, shimmering, flat needles of a salt. The compound therefore forms two salts, $NO_2\cdot C_6H_4\cdot NH\cdot N{:}CMe\cdot C_6H_4\cdot N(NO)\cdot ONa$ (yellow solutions) and $NaO\cdot NO{:}C_6H_4{:}N\cdot N{:}CMe\cdot C_6H_4\cdot N(NO)\cdot ONa$ (blood-red solutions).

The rearrangement of the nitroamine into nitroanilines was effected by adding the fine powder to 62% sulphuric acid at −15°. The solution was poured on ice and the solid product was washed with cold water until free from the diazonium salt (extract A.) and then distilled

in steam. Pale yellow crystals collected first, followed by a golden-yellow solution. The process was prolonged until the distillate was only pale yellow, when the large volume of liquid which collected was left to evaporate and then extracted with ether. The distillate contained 3-*nitro*-2-*aminoacetophenone*, $NO_2 \cdot C_6H_3Ac \cdot NH_2$, which forms very long, golden-yellow, highly refractive, brittle needles, m. p. 92·5—93°. It gives a violet-red azo-dye with α-naphthol, and it is reduced by zinc and sulphuric acid to an *o*-phenylenediamine (ferric chloride reaction). It forms a *semicarbazone*, $C_9H_{11}O_3N_5$, m. p. 223°, which crystallises from hot glacial acetic acid in golden-yellow prisms, and from alcohol, when quickly cooled, as a scarlet powder. The yellow form changes into the red when exposed to moisture or a trace of ammonia, and the red changes to the yellow with a trace of glacial acetic or formic acid. The residue from the steam distillation contained the isomeric nitroaniline, but this was best isolated from the above washings, A, of the crude mixture. This solution was extracted with ether, the extract washed with water and dilute sodium hydroxide, and then the residue after evaporation was treated with steam. The non-volatile part was clarified by animal charcoal, when the filtrate deposited 5-*nitro*-2-*aminoacetophenone* in straw-yellow, silky needles, m. p. 150—151°. It gives a pure blue azo-dye with α-naphthol, and the reduction product, a *p*-phenylenediamine, gives a deep blue colour with oxidising agents, even in very dilute solution. The aqueous and alkaline washings contained traces of the diazonium salts of these nitroanilines and of *o*-aminoacetophenone, and also of *o*-aminoacetophenone itself (acetyl compound isolated) and probably acetophenone.

When a cold solution of *o*-nitroaminoacetophenone is treated with a dilute solution of bleaching powder, a deep flocculent mass of lemon-yellow crystals may be obtained, which has the reactions of a chloroimide, $C_6H_4Ac \cdot NCl \cdot NO_2$. This very readily undergoes rearrangement when boiled with water into the isomeric chloronitroanilines, which are separated by distillation in steam. The volatile 5-*chloro*-3-*nitro*-2-*aminoacetophenone*, $C_8H_7O_3N_2Cl$, forms pale orange, felted needles, m. p. 142—143°, and the isomeric 3-*chloro*-5-*nitro*-2-*aminoacetophenone*, pale yellow, silky needles. These behave like the above non-chlorinated analogues. The reaction with bleaching powder is a delicate test for *o*-nitroaminoacetophenone.

Action of sodium nitrite and 23% *hydrochloric acid on anthranil.*—As it was stated above, the chief product of this reaction is *o*-aldehydophenylnitrosohydroxylamine, but enough of a by-product (compare A., 1909, i, 509; 1911, i, 60) has been accumulated to enable the author to establish it as *o-nitroaminobenzaldehyde*, $CHO \cdot C_6H_4 \cdot NH \cdot NO_2$. This crystallises from water in colourless, silky needles, m. p. 69—70°, and is quite stable in the dark. It reacts with phenylhydrazine and *p*-nitrophenylhydrazine like the above *o*-nitroaminoacetophenone, reduces ammoniacal silver nitrate, gives a deep violet colour when a mixture with α-naphthylamine acetate solution is stirred with a zinc rod, and is reduced by dilute sodium nitrite and metaphosphoric or acetic acid to the diazonium salt which yields salicylaldehyde on boiling. It undergoes rearrangement into 3- and 5-nitro-2-aminobenzaldehydes on boiling with 2*N*-sulphuric acid, and also behaves like the above homologue

towards bleaching powder, but the changes could only be followed by colour reactions, owing to lack of material. J. C. W.

Syntheses by means of Mixed Organo-metallic Derivatives of Zinc. γ-Chloro-ketones and Their Transformation Products. III. HENRI WOHLGEMUTH (*Ann. Chim.*, 1914, [ix], **3**, 141—193. Compare A., 1914, i, 800, 929; this vol., i, 116, 164).—A study of the behaviour of γ-chloro-ketones towards solid potassium hydroxide, diethylamine, mixed organo-magnesium compounds, and potassium cyanide in acid solution.

When γ-chloro-ketones are heated at 140—170° with an excess of solid potassium hydroxide, a molecule of hydrogen chloride is eliminated and a trimethylenic ketone obtained (compare Lipp, A., 1889, 843). Thus ethyl γ-chlorobutyl ketone when heated with solid potassium hydroxide for two hours at 140—150° gives 2-*methyl*cyclo*propyl ethyl ketone*, $C_2H_5\cdot CO\cdot CH\!<\!\begin{matrix}CH_2\\CHMe\end{matrix}\!>CH_2$, b. p. 144—145°/760 mm., having a penetrating odour. It gives an *oxime*, b. p. 99—100°/15 mm., and a *semicarbazone*, white plates, m. p. 96°. Phenyl γ-chlorobutyl ketone under similar conditions yields *methyl*cyclo*propyl phenyl ketone* (2-*benzoyl*-1-*methyltrimethylene*), $COPh\cdot CH\!<\!\begin{matrix}CH_2\\CHMe\end{matrix}\!>CH_2$, b. p. 121°/10·5 mm. This ketone is best purified by preparing its *semicarbazone*, m. p. 187°, and hydrolysing this by dilute sulphuric acid. The ketone gives a p-*nitrophenylhydrazone*, m. p. 109°.

p-Tolyl γ-chloropropyl ketone with potassium hydroxide gives cyclo*propyl* p-*tolyl ketone*, $\begin{matrix}CH_2\\CH_2\end{matrix}\!>CH\cdot CO\cdot C_6H_4Me$, m. p. 48°, best purified by means of its *semicarbazone*, m. p. 208—209°.

On oxidising methyl*cyclo*propyl ethyl ketone with 5% aqueous potassium permanganate in quantity sufficient to give either three or six atoms of oxygen for each molecule of ketone the product in either case is *methyl*cyclo*propylglyoxylic acid*, $\begin{matrix}CH_2\\CHMe\end{matrix}\!>CH\cdot CO\cdot CO_2H$, a slightly oily liquid, b. p. 100—101°/17 mm., which is stable towards 5% potassium permanganate even at 100°. It gives a *semicarbazone*, m. p. 174°, and a *phenylhydrazone*, m. p. 133°. On oxidation with hydrogen peroxide (30 vols.) in aqueous solution, this glyoxylic acid gives methyl*cyclo*propanecarboxylic acid, b. p. 96·5°/14 mm., D_4^{20} 1·0267, n_α 1·43745, n_D 1·44112, n_β 1·44753 (compare Marburg, A., 1897, i, 140). It gave a calcium salt, a *chloride*, b. p. 39·5°/15 mm., and an *anilide*, white needles, m. p. 113·5°.

Diethylamine reacts with γ-chloro-ketones to give the corresponding γ-diethylamino-ketones, the action proceeding much more easily and giving a better yield in the case of ethyl γ-chloropropyl ketone, where the chlorine is attached to a primary carbon atom, than with other ketones, where it is attached to a secondary carbon atom, there being secondary formation of the corresponding *cyclo*propyl ketone. The ketone and the base are heated in a sealed tube at 150° for sixteen hours. In this way, ethyl γ-chlorobutyl ketone yields a certain amount of methyl*cyclo*-

propyl ethyl ketone, together with *ethyl γ-diethylaminobutyl ketone*, $CHMe(NEt_2)\cdot CH_2\cdot CH_2\cdot COEt$, b. p. 101—103°/12 mm., which gives a *hydrochloride* and a *semicarbazone*, m. p. 144°. Ethyl γ-chloropropyl ketone in the same way gives *ethyl γ-diethylaminopropyl ketone*,

$$NEt_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot COEt,$$

b. p. 102°/17 mm. or 95—96°/11 mm., furnishing a *semicarbazone*, m. p. 108°, and on reduction with sodium amalgam in neutral or slightly acid medium, *ζ-diethylaminohexan-γ-ol*,

$$NEt_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHEt\cdot OH,$$

b. p. 110°/14·5 mm., giving a *phenylurethane hydrochloride*, m. p. 99°, and a *benzoic* ester, b. p. 182°/12 mm.

Attempts to prepare magnesium derivatives of ethyl γ-chlorobutyl ketone were not successful.

The γ-chloro-ketones react with mixed organo-magnesium derivatives, giving γ-chloro-tertiary alcohols, which slowly change on keeping or rapidly in contact with alkalis, losing one molecule of hydrogen chloride and giving the corresponding alkyltetrahydrofurans. Thus when magnesium ethyl bromide is run, drop by drop, into ethyl γ-chlorobutyl ketone, *ζ-chloro-γ-ethylheptan-γ-ol*,

$$CHMeCl\cdot CH_2\cdot CH_2\cdot CEt_2\cdot OH,$$

a colourless, mobile liquid, b. p. 108—109°/12 mm., is obtained, which on warming with aqueous potassium hydroxide yields *2-methyl-5 : 5-diethyltetrahydrofuran*, $\begin{matrix} CH_2\text{—}CEt_2 \\ | \\ CH_2\cdot CHMe \end{matrix}\!\!>O$, b. p. 151—152°. Under similar conditions, ethyl γ-chloropropyl ketone yields *ζ-chloro-γ-ethylhexan-γ-ol*, $CH_2Cl\cdot CH_2\cdot CH_2\cdot CEt_2\cdot OH$, b. p. 99—100°/10 mm., which is converted by alkalis into *2 : 2-diethyltetrahydrofuran*, $\begin{matrix} CH_2\cdot CEt_2 \\ | \\ CH_2\text{—}CH_2 \end{matrix}\!\!>O$, a colourless, mobile liquid, b. p. 144—145°.

With potassium cyanide in aqueous solution, the γ-chloro-ketones on the addition of hydrochloric acid yield the corresponding cyanohydrins, which on hydration with concentrated hydrochloric acid followed by the action of potassium hydroxide give the corresponding tetrahydrofurancarboxylic acids. The formation of the cyanohydrin takes several days with continual stirring, the cyanohydrin being extracted with ether. Ethyl γ-chlorobutyl ketone yields *δ-chloro-α-hydroxy-α-ethylhexonitrile*, $CHMeCl\cdot CH_2\cdot CH_2\cdot CEt(OH)\cdot CN$, a viscous liquid, b. p. 151—152°/14 mm. If this nitrile is warmed with 30% aqueous potassium hydroxide, after the addition of alcohol, for eight hours under a reflux condenser, *2-methyl-5-ethyltetrahydrofuran-5-carboxylamide*,

$$\begin{matrix} CH_2\cdot CEt(CO\cdot NH_2) \\ | \\ CH_2\cdot CHMe\text{———} \end{matrix}\!\!>O,$$

is obtained, m. p. 69°. If the hydrolysis is conducted as stated, first with hydrochloric acid and then with potassium hydroxide, *2-methyl-5-ethyltetrahydrofuran-5-carboxylic acid*,

$$\begin{matrix} CH_2\cdot CEt(CO_2H) \\ | \\ CH_2\cdot CHMe\text{———} \end{matrix}\!\!>O,$$

b. p. 116—117°/11 mm., is obtained, giving an *ethyl* ester, b. p. 84°/9·5 mm. In the same way, ethyl γ-chloropropyl ketone yields *δ-chloro-α-hydroxy-α-ethylvaleronitrile*, $CH_2Cl\cdot CH_2\cdot CH_2\cdot CEt(OH)\cdot CN$, a colour-

less, viscous liquid, b. p. 154—155°/19 mm., which on hydrolysis gives *2-ethyltetrahydrofuran-2-carboxylic acid*, $\begin{matrix}CH_2\cdot CEt(CO_2H)\\ |\\ CH_2\cdot CH_2\end{matrix}\!\!>\!O$, b. p. 126—127°/16—17 mm., or 234—235°/755 mm., yielding an *ethyl* ester, b. p. 82—83°/10 mm. W. G.

Steric Hindrance of Chemical Reactions. V. Di-ψ-cumyl Ketone. F. Wenzel [and Franz Wobisch] (*Monatsh.*, 1914, **35**, 987—995).—Although di-ψ-cumylmethane is formed in only small yield by the condensation of ψ-cumene with methylene chloride and cannot be oxidised to the corresponding ketone, the latter substance is readily obtained by the interaction of carbonyl chloride and ψ-cumene in the presence of aluminium chloride.

Di-ψ-cumyl ketone (2 : 4 : 5 : 2′ : 4′ : 5′-*hexamethylbenzophenone*) crystallises in white needles and does not react with phenylhydrazine, hydroxylamine or sodium hydrogen sulphite. Its relationship to di-ψ-cumylmethane (this vol., i, 514) has been established by its conversion into the latter compound on reduction with hydriodic acid and red phosphorus at 200°. When dissolved in a sulphuric acid solution of ammonium nitrate it yields a *tetranitro*-derivative, m. p. 250°.

2 : 4 : 5 : 2′ : 4′ : 5′-*Hexamethylbenzhydrol*, prepared by reducing the ketone with sodium amalgam and alcohol, crystallises in colourless, transparent needles, m. p. 155°, gives an intense red coloration with sulphuric acid, and yields an *acetyl* derivative, m. p. 106°. F. B.

Constitution of Phenyl-*o*-nitroindone and its Decomposition Products. M. Bakunin and T. Angrisani (*Gazzetta*, 1915, **45**, i, 197—204).—Of the three phenylnitroindones, only the ortho-derivative gives an appreciable yield of a solid, crystallisable ozonide with a sharp melting point, whilst the ozonides of the meta- and para-compounds are largely decomposed during ozonisation, the portions which apparently contain the ozonides being syrupy or semi-solid and readily decomposable by heat (this vol., i, 145, 146). It is probable that the position of the nitro-group influences the stability, but the necessity of treating the suspensions of the meta- and para-compounds in chloroform with ozone, owing to their sparing solubility in this solvent in the cold, would render more intense the progressive oxidising and disaggregating action on the small dissolved quantities.

The compound, m. p. 136—137°, obtained by treating phenyl-*o*-nitroindone with barium hydroxide and subsequently adding acid (A., 1912, i, 344), is now found to have m. p. 138—139°, and to be recoverable unchanged from solution in various solvents. It is found further that compounds of identical composition and properties are obtainable by crystallising a mixture in molecular proportions of benzoic and *m*-nitrobenzoic acids from different solvents. The compound is decomposed into its constituents by conversion into the barium salt, the less soluble barium *m*-nitrobenzoate separating, whilst barium benzoate remains in solution. Cryoscopic determination of the molecular weight gives the values, 222—242 in benzene, 139—144 in

acetic acid, and 133—156 in veratrole, the value corresponding with $NO_2 \cdot C_6H_4 \cdot CO_2H, Ph \cdot CO_2H$ being 289.

[With QUERCIGH.]—Thermal investigation of the system benzoic–*m*-nitrobenzoic acids indicates that simple fusion of a mixture of the components in molecular proportions yields this compound, which melts unchanged at 139°, and is moderately stable at a high temperature. T. H. P.

Synthesis of 2-Methyl-1-hydrindone by the Action of α-Bromo*iso*butyl Bromide on Benzene in Presence of Aluminium Chloride. N. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1411—1427).—The action of α-bromo*iso*butyl bromide on benzene in presence of aluminium chloride should yield the bromo-ketone, $CMe_2Br \cdot COPh$, and this, when treated with alcoholic potassium hydroxide, the unsaturated ketone, $CH_2{:}CMe \cdot COPh$. The principal product of these reactions is, however, found to be 2-methyl-1-hydrindone, which is accompanied by the unsaturated ketone in amount too small to permit of its isolation in the pure state. The formation of 2-methyl-1-hydrindone may take place by one of three methods: (1) ring-closure, accompanied by loss of hydrogen bromide in the saturated bromo-ketone, (*a*) with direct production of the hydrindone, or (*b*) with initial formation of $C_6H_4<\begin{matrix}CO\\|\\CMe_2\end{matrix}$, the four-membered ring of which then undergoes conversion into a five-membered ring; (2) isomerisation of the unsaturated ketone,

$$CH_2{:}CMe \cdot COPh.$$

When treated with fuming hydrobromic acid, 2-methyl-1-hydrindone yields a heavy, oily, unstable compound, $C_{10}H_{10}O<\begin{matrix}H\\|\\Br\end{matrix}$. Under similar conditions, 2-methyl-1-hydrindone containing the unsaturated ketone yields, in addition, a *compound*, $C_{20}H_{22}O_3$, which forms hexagonal plates, m. p. 190°, having the normal molecular weight in freezing benzene or boiling chloroform, and remaining unchanged when treated with acetic anhydride, phenylhydrazine, bromine, or concentrated ammonia solution in a sealed tube at 210°. This compound is evidently formed by hydration of 2-methyl-1-hydrindone: $2C_{10}H_{10}O + H_2O = C_{20}H_{22}O_3$. With fuming nitric acid it undergoes hydration and nitration, giving the *compound*, $C_{10}H_{10}O_2(NO_2)_2$, which forms crystals, m. p. 64°, and exhibits normal ebullioscopic behaviour in ether.

2-Methyl-1-hydrindone, b. p. 249°/759 mm., 153°/45 mm., 149°/36 mm., 144°/34 mm., 136°/22 mm., D_0^{20} 1·0640, n_D^{20} 1·5543, has been converted into the oxime, semicarbazone, and hydrazone, and into 2-methyl-1-hydrindamine (compare Kipping and Clarke, T., 1903, **83**, 913). On reduction with sodium in alcoholic solution it yields 2-*methyl*-1-*hydrindol*, $C_6H_4<\begin{matrix}CH(OH)\\|\\CH_2\end{matrix}>CHMe$, b. p. 243°/750 mm., and this, with hydriodic acid, gives 2-*methylhydrindane*, $C_6H_4<\begin{matrix}CH_2\\|\\CH_2\end{matrix}>CHMe$, b. p. 183—185°/747 mm., D_0^{17} 0·9034, n_D 1·5070; the high value of the specific gravity of this hydrocarbon is conditioned by the presence of

the aromatic nucleus, octahydrindene having the value D_0^{20} 0·8334 (compare Ipatiev, A., 1913, i, 1165).

2-*Bromo*-2-*methyl*-1-*hydrindone*, $C_6H_4<^{CO-}_{CH_2}>CMeBr$, forms large, rectangular plates, m. p. 71—72°, and on treatment with *p*-bromophenylhydrazine yields the p-*bromophenylhydrazone*, $C_6H_4<^{C(:N_2H\cdot C_6H_4Br)}_{CH_2}>C:CH_2$ or $C_6H_4<^{C(:N_2H\cdot C_6H_4Br)}_{CH}>CMe$, m. p. 122—123°.

2-*Hydroxy*-2-*methyl*-1-*hydrindone*, $C_6H_4<^{CO-}_{CH_2}>CMe\cdot OH$, forms colourless, rhombic plates or large rhombohedra, m. p. 57°, and yields a *semicarbazone*, $C_{10}H_{10}O:N_2H\cdot CO\cdot NH_2$, m. p. 169°.

Phenyl iso*propenyl ketone*, $CH_2:CMe\cdot COPh$ (?), b. p. 240—244°, D_0^{20} 1·051, was not obtained pure. T. H. P.

Condensation of α-Naphthyl Methyl Ketone with Benzaldehyde. Alexander Albrecht (*Monatsh.*, 1914, **35**, 1493—1506). —*α-Naphthyl styryl ketone*, $C_{10}H_7\cdot CO\cdot CH:CHPh$, prepared by the condensation of α-naphthyl methyl ketone with benzaldehyde by means of aqueous sodium hydroxide in alcohol solution, crystallises in light yellow platelets, m. p. 105°, gives a blood-red coloration with sulphuric acid, and is readily resolved by alcoholic potassium hydroxide into its components. It is accompanied by a yellow oily substance, which resembles the crystalline ketone in general behaviour and is therefore regarded as a stereoisomeride of the *cis-trans*-type. The two isomerides are also formed when the condensation is effected by means of hydrogen chloride or hydrogen bromide. The crystalline ketone yields a *dibromide* crystallising in colourless needles, m. p. 173°, and is reduced by zinc dust and glacial acetic acid to *α-naphthyl β-phenylethyl ketone*, $C_{10}H_7\cdot CO\cdot CH_2\cdot CH_2Ph$, which forms colourless, lustrous, silky platelets, m. p. 93°, and yields an *oxime*, m. p. 120°. 1 : 5-*Diphenyl*-3-*α-naphthyl-pyrazoline*, $C_{10}H_7\cdot C<^{N---NPh}_{CH_2\cdot CHPh}$, prepared by heating α-naphthyl styryl ketone with phenylhydrazine hydrochloride in alcoholic solution, forms yellow, lancet-shaped crystals and shows a magnificent yellowish-blue fluorescence in benzene, chloroform, and alcoholic solution. α-Naphthyl styryl ketone reacts with hydroxylamine in alcoholic solution at 50°, yielding 5-*phenyl*-3-*naphthyl*isooxazoline,

$$C_{10}H_7\cdot C<^{N---O}_{CH_2\cdot CHPh}$$

lustrous, slender, silky platelets, m. p. 126°; with hydroxylamine hydrochloride in alcoholic solution it forms an *oxime*, which crystallises in colourless needles, m. p. 168°, and yields an *acetyl* derivative, colourless prisms, m. p. 136°. An attempt to establish the constitution of this oxime by submitting it to the Beckmann transformation, using phosphorus pentachloride in ethereal solution, resulted in the formation of a yellow substance, m. p. 174°, instead of the expected *cinnamo-α-naphthylamide*. For purposes of comparison the latter compound was prepared by the interaction of cinnamoyl chloride and α-naphthylamine; it crystallises in long, yellow needles, m. p. 120°.

The stereoisomeric *α-naphthyl styryl ketone* forms a viscid, honey-yellow oil, which decomposes on distillation even under diminished pressure and, therefore, could not be isolated in a pure condition. It shows the same behaviour towards sulphuric acid and alkalis as the crystalline ketone, and combines with bromine in glacial acetic acid solution, yielding a *dibromide*, colourless rods, m. p. 170°. F. B.

A Product of the Oxidation of Orcinol. F. HENRICH, W. SCHMIDT, and F. ROSSTEUTSCHER (*Ber.*, 1915, **48**, 483—489).—When a solution of orcinol in aqueous potassium hydroxide is exposed to the air, it becomes dark brown, and an oxidation product may be precipitated on acidifying as a viscous mass which can be obtained as a solid by manipulation with water. Sodium hydroxide gives an oil which cannot be solidified. The substance has been recognised as a quinone of pentahydroxydimethyldiphenyl.

Orcinol was dissolved in potassium hydroxide solution, filtered into a large dish, diluted and left for fourteen days. The oxidation *product* was obtained in ruby-red crystals, m. p. 178—181° (decomp.), by rapid crystallisation from dilute alcohol, and it could be purified by precipitation from the barium salt. It lost water at 145°, and the analyses of the two substances and the loss of weight agreed with the formula $C_{14}H_{12}O_5,H_2O$. It formed a *triacetate*, $C_{20}H_{18}O_8$, m. p. 127°.

The compound was suspended in water and reduced by sulphur dioxide to a *pentahydroxydimethyldiphenyl*, $C_{14}H_{14}O_5$, white needles, m. p. 254°, which yielded a *penta-acetate*, $C_{24}H_{24}O_{10}$, m. p. 155°. The determination of the acetyl groups and of the molecular weight of this compound gave the clue to the whole question. The original oxidation product was regained by the action of dilute chromic acid, and it is, therefore, a quinone of the type $(OH)_2C_6H_2Me\cdot C_6HMe(:O)_2\cdot OH$. J. C. W.

Chlorination of Cyclic Ketones with Antimony Pentachloride. ALFRED ECKERT and KARL STEINER (*Monatsh.*, 1915, **36**, 175—189).—The authors have submitted various cyclic ketones to the action of excess of antimony pentachloride at moderate temperatures and have obtained results somewhat different from those of earlier investigators (compare Diehl, A., 1878, 429; Zetter, A., 1878, 510; Merz and Weith, A., 1884, 588). The general procedure was to take a mixture of the substance with fifteen to twenty times its weight of antimony pentachloride and a trace of iodine; after the first vigorous reaction, the mixture was boiled for six to eight hours. The crude chlorination product was in each case at least twice the weight of the ketone taken.

Anthraquinone gave a product consisting mainly of heptachloroanthraquinone and perchlorobenzoylbenzoic acid, together with smaller quantities of tetrachlorophthalic acid and hexachlorobenzene. *Heptachloroanthraquinone* forms yellowish-green needles, m. p. 380°, and perchlorobenzoylbenzoic acid, hexagonal tablets, m. p. 266°. The *chloride* of the latter acid, m. p. 180°, is remarkably stable, and is not affected by water or alcohol in the cold, but when boiled with an excess of methyl alcohol for a few hours is converted into the difficultly saponifiable *methyl* ester, m. p. 213°. The constitution of the acid is proved by heating with sulphuric acid at 200—250°,

when fission into tetrachlorophthalic acid and pentachlorobenzene is effected; a similar fission takes place when the acid is heated with antimony pentachloride, the products being tetrachlorophthalic acid and hexachlorobenzene. By the above changes, therefore, a systematic degradation of anthraquinone can be produced with the stages:

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_4 \longrightarrow C_6Cl_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6Cl_4 \longrightarrow$$

$$C_6Cl_5\cdot CO\cdot C_6Cl_4\cdot CO_2H \longrightarrow C_6Cl_4(CO_2H)_2 + C_6Cl_6.$$

Fluorenone gave almost entirely o-*pentachlorophenyltetrachlorobenzoic acid* (*perchlorophenylbenzoic acid*), $C_6Cl_5\cdot C_6Cl_4\cdot CO_2H$, leaflets, m. p. 264°, together with a little perchlorodiphenyl. With phenanthraquinone it was found advisable to add the antimony pentachloride in two instalments, the reaction product under these conditions being less complex, consisting chiefly of perchlorophenylbenzoic acid.

The main product from xanthone was *octachloroxanthone*,

$$C_6Cl_4\langle\begin{matrix}CO\\O\end{matrix}\rangle C_6Cl_4,$$

pale yellow needles, m. p. 324°, accompanied by pentachlorobenzoic acid and hexachlorobenzene.

Acridone and methylacridone yielded *octachloroacridone*,

$$C_6Cl_4\langle\begin{matrix}CO\\NH\end{matrix}\rangle C_6Cl_4,$$

pale yellowish-green needles, m. p. 340°. D. F. T.

Exhaustive Halogenation of Anthraquinone. Alfred Eckert and Karl Steiner (*Monatsh.*, 1915, **36**, 269—280. Compare preceding abstract).—The heptachloroanthraquinone obtained by the action of antimony pentachloride on anthraquinone (*loc. cit.*) is not, as was at first thought, 1 : 2 : 4 : 5 : 6 : 7 : 8-heptachloroanthraquinone, synthesis of a compound of this structure yielding a product distinct from it; it must, therefore, be 1 : 2 : 3 : 5 : 6 : 7 : 8-heptachloroanthraquinone, and the apparent difficulty of the occurrence of 1 : 4 : 5 : 8-tetrachloroanthraquinone as an intermediate product is removed by the discovery that treatment of the tetrachloro-compound with antimony pentachloride gives largely the 1 : 2 : 3 : 5 : 6 : 7 : 8-heptachloroanthraquinone instead of the expected 1 : 2 : 4 : 5 : 6 : 7 : 8-isomeride. No success was obtained in an endeavour to produce an analogous brominating effect with antimony tribromide and bromine.

Tetrachlorophthalic anhydride was caused to condense with 1 : 2 : 4-trichlorobenzene in the presence of aluminium chloride, the resulting mixture of isomeric heptachlorobenzoylbenzoic acids, m. p. 226—230°, being accompanied by a neutral *substance*, needles, m. p. 312°. When heated with fuming sulphuric acid at 200° the mixture of heptachlorobenzoylbenzoic acids was converted into 1 : 2 : 4 : 5 : 6 : 7 : 8-*heptachloroanthraquinone*, pale yellow needles, m. p. 302°. Under the influence of antimony pentachloride this compound undergoes partial isomerisation into the 1 : 2 : 3 : 5 : 6 : 7 : 8-compound, and its formation probably precedes that of the latter substance in the exhaustive chlorination of anthraquinone.

By the gradual and cautious addition of bromine to a solution of anthraquinone in fuming sulphuric acid, the mixture being subsequently warmed for three hours at 50°, *heptabromoanthraquinone*,

yellow needles, m. p. above 400°, is obtained. The result is different if an excess of bromine is used at a higher temperature, the reaction product in this case containing *heptabromobenzoylbenzoic* acid, needles, m. p. 278°, and its decomposition products, tetrabromophthalic acid and hexabromobenzene, the m. p. of which was found to be 306° instead of above 315° as generally stated in the literature. When heated with concentrated sulphuric acid, heptabromobenzoylbenzoic acid behaves similarly to its chlorine analogue, yielding tetrabromophthalic acid and pentabromobenzene; the latter substance, silky needles, m. p. 293°, appears not to have been obtained pure by previous investigators.

D. F. T.

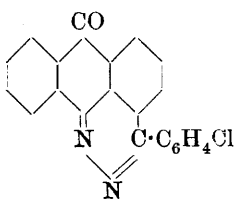
Benzoylanthraquinones. ALFRED SCHAARSCHMIDT (*Ber.*, 1915, **48**, 831—839).—The condensation of the chloride of 1- or 2-anthraquinonecarboxylic acid with benzene in the presence of aluminium chloride produces the corresponding 1- and 2-benzoylanthraquinones; these compounds, however, cannot be obtained by the condensation of benzoyl chloride with anthraquinone, neither does the indirect process of first condensing benzoyl chloride with anthracene give encouraging results.

The chloride of 2-anthraquinonecarboxylic acid condenses readily with aromatic hydrocarbons with satisfactory results, but the isomeric chloride derived from 1-anthraquinonecarboxylic acid and, in a still more marked manner, the resulting 1-benzoylanthraquinone are very sensitive towards aluminium chloride, so that the yield is poor.

Anthraquinone-1-carboxylic acid was converted into its chloride by boiling in benzene solution with phosphorus pentachloride; the product condenses with chlorobenzene in the presence of aluminium chloride, producing 1-p-*chlorobenzoylanthraquinone*,

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_3\cdot CO\cdot C_6H_4Cl,$$

pale brownish-yellow plates, m. p. 238°, which is accompanied by a colourless *substance* (possibly the isomeric 1-*o*-chlorobenzoylanthraquinone), m. p. 177°. In a similar manner, condensation of the acid chloride with benzene, toluene, and anisole gave respectively 1-*benzoylanthraquinone*, $C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_3\cdot CO\cdot C_6H_5$, a yellowish-white powder, m. p. 229°, 1-p-*toluoylanthraquinone*, $C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_3\cdot CO\cdot C_6H_4Me$, stout, colourless plates, m. p. 200°, and 1-p-*methoxybenzoylanthraquinone*, $C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_3\cdot CO\cdot C_6H_4\cdot OMe$, m. p. 269°. These products, in the manner of 1 : 4-diketones, condense with hydrazine, giving *o*-diazines; the compound (annexed formula) obtained from 1-*p*-chlorobenzoylanthraquinone and hydrazine forms yellow needles, m. p. above 300°. They also dissolve in aqueous sodium hyposulphite solution, giving red solutions.



Condensation of the chloride of 2-anthraquinonecarboxylic acid with toluene yielded

2-p-*toluoylanthraquinone*, m. p. 181—182°, which on reduction with sodium hyposulphite gives a green solution, whereas the corresponding *product* from *m*-chlorotoluene and the same acid chloride gave a reddish-brown solution. The chloride of 1-chloroanthraquinone-2-carboxylic acid underwent condensation with toluene, forming 1-*chloro*-2-*toluoylanthraquinone*, pale brown crystals, m. p. 193°, which gave a reddish-brown solution with aqueous alkaline sodium hyposulphite.

The most marked distinction between the 1-benzoyl- and 2-benzoylanthraquinone compounds is in the behaviour of the former on reduction in acid solution, treatment in solution in sulphuric acid with a little copper or aluminium bronze or a little zinc dust, giving an intense green liquid which on dilution gives a violet precipitate; the isomeric 2-benzoylanthraquinones do not give this colour reaction.

D. F. T.

Anthrimides [Dianthraquinonylamines]. Alfred Eckert and Karl Steiner (*Monatsh.*, 1914, **35**, 1129—1151).—An account of the preparation and properties of the three isomeric dianthraquinonylamines and their nitro-derivatives. On reduction with stannous chloride in alkaline solution the nitro-derivatives are converted into the corresponding hydroxy-compounds, the nitro-groups being eliminated during the reduction in the form of ammonia. Reduction in acid solution results in the formation of the corresponding amino-compounds or of indanthren derivatives.

1 : 1′-Dianthraquinonylamine, $(C_6H_4{:}C_2O_2{:}C_6H_3)_2NH$, prepared by heating 1-aminoanthraquinone and 1-chloroanthraquinone with sodium acetate and metallic copper in nitrobenzene solution at 200° (compare D.R.-P. 162824) crystallises in dark red needles, and gives an olive-green coloration with sulphuric acid; the *benzoyl* derivative forms yellow needles.

1 : 2′-*Dianthraquinonylamine*, obtained from 1-chloroanthraquinone and 2-aminoanthraquinone or from 2-chloroanthraquinone and 1-aminoanthraquinone in a similar manner, crystallises in coppery-red needles.

2 : 2′-Dianthraquinonylamine, prepared by heating 2-chloroanthraquinone and 2-aminoanthraquinone with potassium carbonate at 280°, forms pale coppery-red needles (compare D.R.-P. 257811).

When mixed with sodium hydrogen carbonate and exposed for two to three days to the action of bromine vapour at the ordinary temperature, 1 : 1′-dianthraquinonylamine yields 4 : 4′-*dibromo*-1 : 1′-*dianthraquinonylamine*, which forms dark red needles, sublimes undecomposed, and reacts with boiling aniline in the presence of sodium carbonate and a trace of cuprous chloride to form 4 : 4′-*dianilino*-1 : 1′-*dianthraquinonylamine*, $(C_6H_4{:}C_2O_2{:}C_6H_2{\cdot}NHPh)_2NH$, crystallising in dark bluish-green needles.

4 : 4′-*Dinitro*-1 : 1′-*dianthraquinonylamine*, prepared by nitrating 1 : 1′-dianthraquinonylamine with the calculated amount of acid in a sulphuric acid solution of boric acid, forms small, brownish-red scales, and reacts with aniline in the presence of sodium carbonate, yielding the dianilino-derivative mentioned above. The constitution of the dinitro-compound has been established by its formation from 1-amino-

4-nitroanthraquinone and 1-chloro-4-nitroanthraquinone by heating the components in nitrobenzene solution in the presence of potassium carbonate and cuprous chloride.

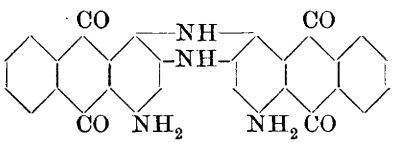
1-Chloro-4-nitroanthraquinone, prepared by nitrating 1-chloroanthraquinone, forms large, yellow crystals, m. p. 259°, and when heated with *p*-toluidine in the presence of stannous chloride, sodium carbonate and boric acid is converted into 1 : 4-di-*p*-toluidinoanthraquinone, long, blue needles, m. p. 213° (D.R.-P. 91149). When heated with nitric acid (D 1·5) on the water-bath, 1 : 1′-dianthraquinonylamine yields 2 : 2′ : 4 : 4′-*tetranitro*-1 : 1′-*dianthraquinonylamine*, which crystallises in reddish-orange needles and is probably identical with the nitro-derivative described in D.R.-P. 213501.

1 : 4-*Dinitro*-1 : 2′-*dianthraquinonylamine*, orange leaflets, and 2 : 4 : 1′-*trinitro*-1 : 2′-*dianthraquinonylamine*, yellow needles, are also described.

On reduction with alkaline stannous chloride, 4 : 4′-dinitro-1 : 1′-dianthraquinonylamine yields 4 : 4′-*dihydroxy*-1 : 1′-*dianthraquinonylamine*, crystallising in violet needles. The constitution of the dihydroxy-compound has been confirmed by its formation from 1-chloro-4-hydroxyanthraquinone and 1-amino-4-hydroxyanthraquinone in hot nitrobenzene solution in the presence of a copper salt.

1-*Nitro*-4-*hydroxyanthraquinone*, prepared by nitrating 1-hydroxyanthraquinone in a sulphuric acid solution of boric acid, crystallises in golden-yellow needles, m. p. 267°, and is reduced by sodium sulphide to 1-amino-4-hydroxyanthraquinone (Schmidt and Gattermann, A., 1897, i, 196).

1-*Chloro*-4-*hydroxyanthraquinone* is obtained in orange-yellow needles, m. p. 186°, by the addition of hydrochloric acid to a suspension of 1-hydroxyanthraquinone in a dilute acetic acid solution of sodium chlorate. When heated with methyl alcohol and potassium hydroxide at 100° it yields 4-*methoxy*-1-*hydroxyanthraquinone* (*quinizarin monomethyl ether*), which forms yellow needles, m. p. 189°, and is hydrolysed by sulphuric acid in the presence of boric acid at 140° to quinizarin.



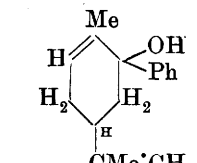
2 : 2′-*Diamino*-4 : 4′-*dihydroxy*-1 : 1′-*dianthraquinonylamine*, prepared by reducing 4 : 4′ : 2 : 2′-tetranitro-1 : 1′-dianthraquinonylamine with alkaline stannous chloride or sodium sulphide, crystallises in microscopic, dark green needles; reduction with stannous chloride and hydrochloric acid in acetic acid solution yields 4 : 4′-*diaminoindanthren* (annexed formula), small, green needles.

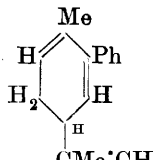
1′ : 4-*Dihydroxy*-1 : 2′-*dianthraquinonylamine*, prepared from the corresponding dinitro-derivative by reducing with alkaline stannous chloride, forms brownish-red crystals; reduction in acid solution yields 1′ : 4-*diamino*-1 : 2′-*dianthraquinonylamine*, lustrous, brown crystals.

Alkaline reduction of 2 : 4 : 1′-trinitro-1 : 2′-dianthraquinonylamine gives rise to 2-*amino*-1′ : 4-*dihydroxy*-1 : 2′-*dianthraquinonylamine*, as an amorphous, brown powder. F. B.

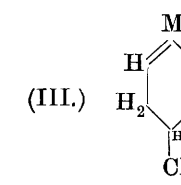
Higher Molecular, Optically Active Hydrocarbons and Ketones from Carvone. H. Rupe and W. Tomi (*Ber.*, 1914, **47**, 3064—3083).—An account of further reactions between carvone and organo-magnesium haloids (compare Rupe and others, A., 1906, i, 374; 1908, i, 433; Klages and Sommer, A., 1906, i, 566; Auwers and Eisenlohr, A., 1910, ii, 367).

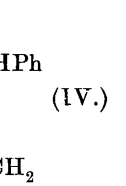
Carvone and magnesium phenyl bromide yielded 2-*phenyl*-$\Delta^{6:8}$-p-*menthadiene*-2-*ol* [2-*phenylcarveol*] (I.) as a viscous oil, b. p. 164·5—165·5°/10 mm., α_D^{15} +134·5°, probably isomeric with a carbinol obtained under the same conditions by Klages (*loc. cit.*). Attempts to convert this into a hydrocarbon by the elimination of water failed, so Klages' directions were followed in order to prepare one directly from carvone. An oil was obtained with b. p. 149—150°/10 mm., α_D^{15} +65·32°, D_4^{20} 0·9714, n_α 1·56106, n_D 1·56736, n_β 1·58273, n_γ 1·59686, whereas Klages found α_D^{15} +134·5°, n_D 1·5631. The present hydrocarbon is therefore an isomeride, probably 2-*phenyl*-$\Delta^{2:6:8}$-p-*menthatriene* (II.). Like Klages' compound, it yielded 2-phenyl-*p*-cymene on inversion.

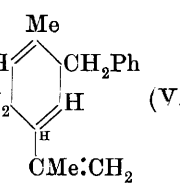

(I.)


(II.)

When carvone is treated with magnesium benzyl chloride, two hydrocarbons and a ketone (the main product) result. It was found, however, that the reaction was inconsistent, for frequently it happened that much water was evolved when the product was distilled, due no doubt to the formation of carbinols. The ketone was frozen out and the oil fractionated. The first fraction contained the *hydrocarbon*, $C_{17}H_{20}$, probably (III), b. p. 162—166°/10 mm., D_4^{20} 0·9651, α_D^{20} +112·52°, n_α 1·55730, n_D 1·56365, n_β 1·57870, n_γ 1·59242; the *isomeride*, probably (IV), was a viscous oil, b. p. 169—173°/10 mm., D_4^{20} 0·9836, α_D^{20} +257·6°, n_α 1·56946, n_D 1·57611, n_β 1·59416, n_γ 1·61076. Both yielded 2-*benzyl*-p-*cymene*, $C_6H_3MePr^\beta{\cdot}CH_2Ph$, on inversion, as an inactive oil, b. p. 165—167°/12 mm., D_4^{20} 0·9628, n_D^{20} 1·55638. The

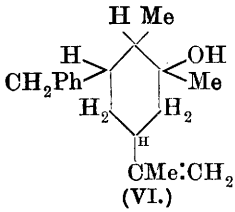

(III.)


(IV.)

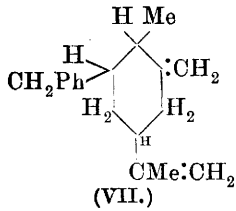

(V.)

main product, 6-*benzyl*-Δ^8-p-*menthene*-2-*one* [6-*benzyldihydrocarvone*] (V), had b. p. 181—184°/11 mm., and formed white needles, m. p. 73°; D_4^{20} of 10% solution in benzene 0·8887, α_D^{20} −1·82°. The *oxime*, $C_{17}H_{23}ON$, had m. p. 140—141°, but semicarbazide gave no semicarbazone, but rather an *additive* compound, $C_{18}H_{27}O_2N_2$.

α-Bromo-α-phenylethane, b. p. 84—86°/10 mm., was prepared from phenylmethylcarbinol, b. p. 91—92°/12 mm., by the action of



(VI.)

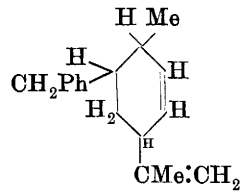


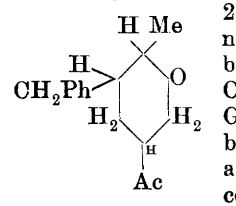
(VII.)

phosphorus tribromide. The magnesium compound of this did not react in the above way with carvone, but gave a mono-molecular, inactive benzenoid *hydrocarbon*, $C_{18}H_{20}$, m. p. 127°.

The above benzyldihydrocarvone (V) also reacts with Grignard reagents. With magnesium methyl iodide it gave 6-*benzyl*-2-*methyl*-Δ^8-p-*menthen*-2-*ol* (VI), b. p. 188—190°/10 mm., which was dehydrated to 6-*benzyl*-2-*methylene*-Δ^8-p-*menthene* (VII) by potassium hydrogen sulphate at 200—210° in a current of hydrogen. The hydrocarbon has b. p. 169—172°/11 mm., D_4^{20} 0·9456, α_D^{20} −0·66°, n_D^{20} 1·54718. Similarly, magnesium propyl bromide gave 6-*benzyl*-2-*propyl*-Δ^8-p-*menthen*-2-*ol*, $C_{20}H_{30}O$, b. p. 204—206°/10 mm., and this, 6-*benzyl*-2-*propylidene*-Δ^8-p-*menthene*, $C_{20}H_{28}$, b. p. 183—186°/13 mm., α_D^{20} −1·10°; magnesium phenyl bromide yielded 2-*phenyl*-6-*benzyl*-Δ^8-p-*menthen*-2-*ol*, $C_{23}H_{28}O$, b. p. 230—240°/13 mm., m. p. 77°, and this, 2-*phenyl*-6-*benzyl*-$\Delta^{2:8}$-p-*menthadiene*, $C_{23}H_{26}$, b. p. 234—237°/13 mm., D_4^{20} of 10% benzene solution 0·8897, α_D^{20} −6·54°; whilst magnesium benzyl chloride formed 2:6-*dibenzyl*-Δ^8-p-*menthen*-2-*ol*, $C_{24}H_{30}O$, m. p. 87°, and this, 2-*benzylidene*-6-*benzyl*-Δ^8-p-*menthene*, $C_{24}H_{28}$, b. p. 232—235°/11 mm., D_4^{20} 1·0015, n_D^{20} 1·58159, α_D^{20} +0·66°.

The same ketone was also treated with phosphorus pentachloride and the crude chloro-derivative reduced by sodium and alcohol. The resulting 6-*benzyl*-$\Delta^{2:8}$-p-*menthadiene* (annexed formula) had b. p. 167—169°/14 mm., α_D^{20} −6·35°, D_4^{20} of 10% benzene solution 0·8850. The ketone was also dissolved in glacial acetic acid and treated with ozone. The solvent and formaldehyde were removed by steam, when the residue solidified on cooling. This was recognised as 4-*acetyl*-6-*benzyl*-1-*methyl*cyclo*hexan*-2-*one* (annexed formula). It forms pleasant smelling needles, m. p. 78°, b. p. 214—220°/12 mm., D_4^{20} of 10% benzene solution, 0·8769, α_D^{20} −8·46°, yields a *dioxime*, $C_{16}H_{22}O_2N_2$, m. p. 195—196°, and reacts with Grignard compounds. The same diketone was formed by oxidation of the substituted carvone by chromic acid or permanganate. Other oxidation products could not be isolated, but the ketone yielded carvacrol by fusion with potassium hydroxide. J. C. W.





Volatile Oils of the Genus Solidago. Emerson R. Miller and Jemison Mims Moseley (*J. Amer. Chem. Soc.*, 1915, **37**, 1285—1294).—On distilling plants of *Solidago rugosa* in a current of steam, 0·4% of a pale yellow oil was obtained which furnished the following constants: D_{25}^{25} 0·8620, α_D −12·8°, n_D^{23} 1·4813, saponification number 4·22, saponification number after acetylation 10·97. This oil is composed chiefly of terpenes, including α-pinene, and probably some

β-pinene and limonene. The oil also seems to contain 1·47% of an ester (calculated as bornyl acetate) and 1·67% of an alcohol (calculated as borneol).

The oil of *Solidago odora*, obtained in a yield of about 1% by distilling the fresh, flowering wild plants in a current of steam, had a pale yellow colour and an anise-like odour, and gave the following constants: D_{25}^{25} 0·9310, α_D +13·72°, n_D^{23} 1·5065, saponification number 7·9, acid number 0·63. From cultivated plants a yield of 0·65% of oil was obtained, which had D_{15}^{25} 0·9450, α_D + 9·33°, n_D^{24} 1·5140, saponification number 8·9, saponification number after acetylation 19·4. The oil of *Solidago odora* contains terpenes, 10—15%; esters, about 3% (calculated as bornyl acetate); alcohols, including borneol, 3% (calculated as borneol); methylchavicol, about 75%; and small quantities of volatile and non-volatile acids. E. G.

Mangostin: a Crystalline Substance Allied to the Resins. John Robertshaw Hill (T., 1915, **107**, 595—601).—Mangostin was first isolated from the skin of the mangosteen fruit by Schmid (*Annalen*, 1865, **93**, 83), who assigned to it the formula $C_{20}H_{22}O_5$.

It has now been found that mangostin has the composition $C_{23}H_{24}O_6$, and that it contains two phenolic hydroxyl groups, one methoxyl group, and one or more amyl groups. The compound crystallises in small, flat, pale yellow needles, but in other respects it resembles the natural resins. It dissolves in solutions of alkali hydroxides to form unstable salts which are decomposed by carbon dioxide; and it reacts with bromine and also with concentrated sulphuric acid, but in neither case can definite products be isolated. When ferric chloride is added to an alcoholic solution of mangostin, a greenish-brown coloration is produced, which is discharged by hydrochloric acid. Mangostin is oxidised by warm nitric acid or by a solution of potassium permanganate with the formation of oxalic acid and other products. On fusion with potassium hydroxide, it yields amyl alcohol, and acetic, valeric, and benzoic acids.

Dimethylmangostin, $C_{25}H_{28}O_6$, m. p. 123° (uncorr.), obtained by shaking a solution of mangostin in dilute potassium hydroxide with excess of methyl sulphate, crystallises in long, faintly yellow, slender, silky needles.

The *compound*, $C_{22}H_{22}O_6$, m. p. 180—181° (uncorr.), obtained by the action of hydriodic acid on mangostin, forms long, very pale yellow, silky needles or short rhombs; a solution of this substance in alcohol gives a deep green coloration with ferric chloride. It yields a *methyl* derivative, m. p. 216° (uncorr.), and an *acetyl* derivative, m. p. 218—219° (uncorr.). E. G.

Convallarin. J. Lindner (*Monatsh.*, 1915, **36**, 257—267).—Little is known of the chemistry of the glucosides convallarin and convallamarin which were first separated from the Lily of the Valley (*Convallaria majalis*) by Walz in 1858 (see Votoček and Vondraček, A., 1904, i, 177; 1906, i, 378; Reichard, A., 1911, ii, 345).

In a re-investigation of a sample of convallarin from a commercial source, the author has been unable to verify Walz's statement that it can be made to assume a crystalline condition, although the material

appeared to be pure. Analysis indicated a formula $C_{25}H_{40}O_{10}$, instead of $C_{34}H_{62}O_{11}$, as suggested by Walz. By heating with dilute sulphuric acid, convallarin is hydrolysed to a hexose and convallaretin, the latter forming crystals which decompose without melting on heating. The formula of convallaretin is probably $C_{19}H_{28}O_4$, this being confirmed by analysis and by molecular-weight determination in phenol. Convallaretin forms a stable monohydrate; it is free from ethylenic linkings, ketonic groups, and methoxyl groups, but contains two hydroxyl radicles; the two remaining oxygen atoms appear to constitute part of a carboxy-ester group. The action of alcoholic potassium hydroxide on convallaretin was not fully investigated, but a *substance*, $C_{18}H_{28}O_4$, was isolated from the product. Although the study of convallaretin could not be completed, the author is able to state with confidence that its constitution must include a benzene ring. D. F. T.

Bixin. J. Herzig and F. Faltis [with E. Mizzan] (*Monatsh.*, 1914, **35**, 997—1020).—The authors find that bixin and its derivatives are difficultly combustible, so that special precautions are necessary in order to obtain correct analytical values. The results of numerous analyses show that bixin and its methyl ether have the formulæ $C_{25}H_{27}O_3{\cdot}OMe$ and $C_{25}H_{26}O_2(OMe)_2$ respectively (compare Heiduschka and Riffart, A., 1911, i, 315; also Hasselt, A., 1911, i, 550). The methoxyl content and also cryoscopic determinations of the molecular weight of bixin in *p*-toluidine and diphenylamine are also in agreement with these formulæ.

The methyl ether, prepared by the action of diazomethane on bixin or of methyl sulphate on its potassium salt, has m. p. 158°.

Dihydrobixin, prepared by reduction with zinc dust and acetic acid, forms reddish-yellow crystals, m. p. 178—179°. Different preparations of the dihydro-derivative show a marked difference in their behaviour on exposure to light and air. Some specimens become almost colourless during the course of twelve to fourteen days, and increase in weight by 30—32%, whilst others remain practically unchanged even after several months' exposure.

In solution, however, all preparations undergo oxidation in the course of three to four days, the increase in weight being 38—40%. Determination of the methoxyl content in the oxidation product, after methylation with diazomethane, shows that one, or at most two, new carboxyl or hydroxyl groups are formed, although the increase in weight corresponds with the addition of eight or ten atoms of oxygen.

According to Hasselt, bixin quantitatively decomposes at 190—200° into *m*-xylene and an amorphous product, $C_{21}H_{24}O_5$. The authors find, however, that the decomposition is much more complicated. The distillate has no constant b. p., although *m*-xylene may be readily isolated from it. Further, the residue, after heating, contains a smaller percentage of methoxyl than bixin itself, whilst substances containing methoxy-groups occur in the volatile products.

Determinations of the iodine value of bixin, its methyl ether, and dihydro-derivative by the methods of Hübl and Wys show that all three compounds combine with eight atoms of iodine, but in the case of the

two first-named substances the addition of the two last iodine atoms proceeds with difficulty. F. B.

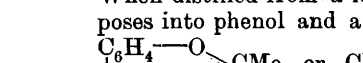
Russian, particularly Caucasian, Tanning Materials. V. G. Povarnin and V. Tolkunov (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1343—1346. Compare A., 1914, i, 241, 242).—The amounts of soluble extract, the proportions of tannides and non-tannides, the colours of the extracts determined with the standard yellow, red and blue glasses of the Lovibond tintometer, etc., are given for a considerable number of tanning materials. The official method for estimating non-tannides does not yield accurate results in cases where the tannides decompose on heating. T. H. P.

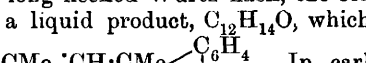
Formation of Furfuraldehyde by the Action of Steam on Wood. Emil Heuser (*Zeitsch. angew. Chem.*, 1914, **27**, 654—655).—The formation of furfuraldehyde was observed when wood or straw was heated with high-pressure steam. Closer investigation of the conditions showed that neither wood nor the active constituent, xylose, was converted into furfuraldehyde by boiling water or steam under atmospheric pressure, but xylose heated with water in a sealed tube at 135—140° for eight hours gave 11·7% of the aldehyde, as estimated by Tollens' phloroglucide method. The addition of acetic and formic acids to the water increased the yield of furfuraldehyde under otherwise identical conditions to 31—32%, so that these acids which are produced at the same time from the wood exert an accelerating influence on the formation of aldehyde, similar to that of hydrochloric acid. An increase in the temperature of the experiment to 160° further increased the yield of furfuraldehyde to 38·5%. G. F. M.

Condensation of Phenol with Unsaturated Ketones: with Mesityl Oxide. A. P. Dianin (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1310—1319).—The author has previously shown (A., 1893, i, 214) that, under the influence of hydrochloric acid, saturated ketones condense with phenol, giving dihydric phenols, with both the hydroxyl groups in the para-position:

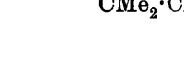
$$R_2{:}CO + 2Ph{\cdot}OH = OH{\cdot}C_6H_4{\cdot}CR_2{\cdot}C_6H_4{\cdot}OH + H_2O.$$

Under similar conditions, phenol and mesityl oxide condense, giving a monohydric phenol: $C_6H_{10}O + 2Ph{\cdot}OH = C_{18}H_{20}O_2 + H_2O$. For this compound, three formulæ are possible:


(I),


(II),

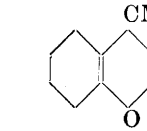
and $OH{\cdot}C_6H_4{\cdot}CMe_2{\cdot}CH_2{\cdot}CMe<\begin{matrix}C_6H_4\\O\end{matrix}$ (III). Fusion with potassium hydroxide yields salicylic acid, and oxidation of its methyl ester with chromic acid gives anisic acid, so that the $\cdot C_6H_4{\cdot}OH$ is a para-group and the $\cdot C_6H_4{\cdot}O\cdot$ an ortho-group; the second formula is thus excluded. When distilled from a long-necked Wurtz flask, the compound decomposes into phenol and a liquid product, $C_{12}H_{14}O$, which may be either


or $CMe_2{:}CH{\cdot}CMe<\begin{matrix}C_6H_4\\O\end{matrix}$. In carbon disulphide

solution, this product reacts with bromine, with evolution of hydrogen bromide, but remains unchanged when treated with alkali or with water, or when its alcoholic solution is heated at 140° in a sealed tube. The conclusion is drawn that it is represented by the first of the two above formulæ, and the original compound by formula I.

The mechanism of the reaction between mesityl oxide and phenol is as follows: $CMe_2{:}CHAc + 2HCl = CMe_2Cl{\cdot}CH_2{\cdot}CMeCl{\cdot}OH$; this $+ 2Ph{\cdot}OH = 2HCl + OH{\cdot}C_6H_4{\cdot}CMe_2{\cdot}CH_2{\cdot}CMe(OH){\cdot}C_6H_4{\cdot}OH$, the latter then undergoing ring-closure with loss of 1 mol. of water.

2-*Hydroxyphenyl*-2 : 4 : 4-*trimethyl*-2 : 3-*dihydrobenzopyran* (annexed formula) (compare Bülow and Wagner, A., 1901, i, 400, 559), m. p. 157·5°, forms the following highly stable, isomorphous, crystalline compounds: $8C_{18}H_{20}O_2,Et_2O$, m. p. 171—172°; $4C_{18}H_{20}O_2,Et{\cdot}OH$, m. p. 163—164°; $4C_{18}H_{20}O_2,CH_3{\cdot}COMe$, $4C_{18}H_{20}O_2,CH_3{\cdot}CO_2H$, and $4C_{18}H_{20}O_2,CHCl_3$. Its *benzoyl* derivative, $C_{18}H_{19}O_2Bz$, forms elongated, rhombic plates, m. p. 161°, and gives an orange-red solution in concentrated sulphuric acid. Its *methyl* ether, $C_{19}H_{22}O_2$, forms crystals, m. p. 36°, b. p. 285—286°, D_4^{19} (liq.) 1·0980, has the normal molecular weight in freezing urethane, and when warmed emits an odour recalling that of bitter almonds; it dissolves in concentrated sulphuric acid giving an orange-red coloration.



2 : 4 : 4-*Trimethylbenzopyran*, $C_{12}H_{14}O$, is a colourless liquid with a characteristic odour, b. p. 235—236° (slight decomp.), 166°/84 mm., D_4^{20} 1·0085, n_D^{20} 1·5450, and has the normal vapour density and the normal molecular weight in freezing urethane. It decolorises dilute permanganate solution slowly, and yields 2-hydroxyphenyl-2 : 4 : 4-trimethyl-2 : 3-dihydrobenzopyran when mixed with phenol and treated with hydrogen chloride.

Preliminary experiments show that mesityl oxide gives analogous decomposition products with other phenols, and that the reaction may be extended to other unsaturated ketones. T. H. P.

Catalytic Reduction of 4-Pyrones. W. Borsche [with A. Mehner] (*Ber.*, 1915, **48**, 682—686).—It was recently found that yangonin, a compound in which a benzene residue is attached to the 2-position of a 4-pyrone ring by an ethylene chain, was only saturated by hydrogen at the ethylene linking when submitted to catalytic reduction (Borsche and Gerhardt, this vol., i, 438). The unexpected result that an $a\beta$-unsaturated ketone, like the pyrone ring, should escape reduction has led the author to test the point. Simple pyrones are found to be reduced easily, but substituents in the 2 : 6-positions seem to have a marked retarding effect on the action.

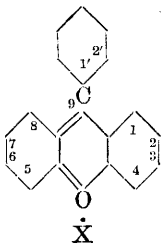
4-Pyrone, b. p. 215—217°, was dissolved in water and shaken with palladium chloride and gum arabic in an atmosphere of hydrogen. The solution was then distilled and the distillate saturated with potassium carbonate. The *tetrahydro*-4-*pyrone*, $O<\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}>CO$,

which separated, was a very volatile, mobile, yellow oil, b. p. 163—166°/742 mm. It was characterised by a *phenylsemicarbazone*, O:$(CH_2)_4$:C:N·NH·CO·NHPh, slender needles, m. p. 169°, a 3 : 5-*dibenzylidene* compound, $O<\begin{matrix}CH_2\cdot C(:CHPh)\\CH_2\cdot C(:CHPh)\end{matrix}>CO$, pale yellow, rhombic leaflets, m. p. 185°, a 3 : 5-*dianisylidene* compound, $C_{21}H_{20}O_4$, slender, yellow needles, m. p. 179—180° (turbid), 222—223° (clear), and a 3 : 5-*dicinnamylidene* compound, $C_{23}H_{20}O_2$, brilliant yellow leaflets, m. p. 213—214°.

2 : 6-Dimethyl-4-pyrone was reduced to 2 : 6-*dimethyltetrahydro*-4-*pyrone*, $C_7H_{12}O_2$, m. p. 170°/737 mm., which formed a *semicarbazone*, $C_8H_{15}O_2N_3$, stout prisms, m. p. 192°, a *phenylsemicarbazone*, O:$(CHMe)_2$:$(CH_2)_2$:C:N·NH·CO·NHPh, long needles, m. p. 211—212°, but no aldehyde derivatives. Ethyl chelidonate was also reduced to *ethyl tetrahydro*-4-*pyrone*-2 : 6-*dicarboxylate* (*ethyl tetrahydrochelidonate*), $CO<\begin{matrix}CH_2\cdot CH(CO_2Et)\\CH_2\cdot CH(CO_2Et)\end{matrix}>O$, b. p. 200—215°/17 mm., m. p. 80—82°, which yielded a *phenylsemicarbazone*, slender needles, m. p. 164°.

A remarkable fact which will be further investigated is that the reduced compounds boil at much lower temperatures than the unsaturated pyrones. J. C. W.

Oxonium Bases which have the Character of Alkalis. F. Kehrmann and Adolf Bohn (*Ber.*, 1914, **47**, 3052—3064. Compare A., 1914, i, 314).—A study of the substitution products of 9-phenylxanthonium (annexed formula) with regard to the resistance of the salts to hydrolysis, has brought to light the following facts. The unsubstituted salts only exist in the solid state or in the presence of a large excess of a strong acid; methyl groups in positions 2 and 7 have little influence, but in 3 and 6 increase the stability at least a hundred-fold; a carboxyl group in 11 lowers the stability again, but an ester group increases it very considerably. Combining the favourable substituents, the compound, methyl 9-phenyl-3 : 6-dimethylxanthonium-2′-carboxylate, was found to give salts of strong acids which could be recrystallised from the very dilute acid (A., 1912, i, 43). If methoxyl be substituted for methyl in 3 and 6, still more stable salts are obtained, so that, finally, the 2 : 3 : 6 : 7-tetramethoxy-2′-carboxylic methyl ester, and some others, are found to give stable hydrogen carbonates and may even be isolated as free bases.

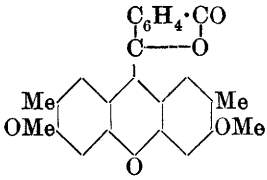


The existence of such stable bases, composed of carbon, hydrogen, and oxygen only, emphasises the enormous influence on the behaviour of a compound which is exerted by the molecular structure compared with that due to the nature of the individual elements.

The *hydrogen carbonate* of *methyl* 3 : 6-*dimethoxy*-9-*phenylxanthonium*-2′-*carboxylate* was briefly mentioned in the earlier paper as a lemon-yellow substance. If a 1% solution of the corresponding chloride is shaken with fresh silver oxide, a yellow, fluorescent solution of the base is obtained. This is alkaline to litmus, but soon deposits the

white lactone, owing to hydrolysis of the methyl ester group, followed by rearrangement.

The condensation product of cresorcinol and phthalic anhydride, namely, *cresorcinolphthalein*, $C_{22}H_{16}O_5$, forms an orange-red, sparkling chloride. This was methylated by methyl sulphate in nitrobenzene at 150°, and after a troublesome purification, the *chloride* of the trimethyl ether ester, *methyl* 3 : 6-*dimethoxy*-9-*phenyl*-2 : 7-*dimethylxanthonium*-2′-*carboxylate*, was obtained as a solid which dissolved completely in water with deep yellow colour and bluish-green fluorescence. The *bromide*, *iodide*, *dichromate*, and *platinichloride* are now mentioned, whilst the hydrogen carbonate was described in the earlier paper. The free *base* was liberated by silver oxide. It is strongly alkaline and tastes bitter. When the solutions are warmed, especially with alkalis, the lactone, 3 : 6-*dimethoxy*-2 : 7-*dimethylfluoran* (annexed formula), separates as a white, crystalline powder, m. p. 278°.



It was also already stated that 2 : 3 : 6 : 7-tetramethoxy-9-phenylxanthonium probably forms a carbonate (A., 1912, i, 1012). The *hydrogen carbonate* has now been isolated in golden-yellow leaflets, and a dilute solution of the free base has also been obtained as above. Similarly, the number of the salts of *methyl* 2 : 3 : 6 : 7-*tetramethoxy*-9-*phenylxanthonium*-2′-*carboxylate* (A., 1913, i, 1352) has been increased by the *chloride*, golden-yellow leaflets, *bromide*, *iodide*, and *carbonate*, orange, crystalline powder, and the free base has been obtained in solution and, by evaporation in a vacuum desiccator, apparently in golden-yellow crystals. J. C. W.

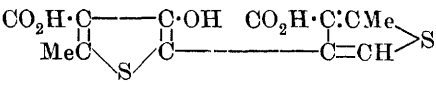
Syntheses of Hydroxythiophen Derivatives from Ethyl Aminocrotonate. Erich Benary and A. Baravian (*Ber.*, 1915, **48**, 593—604).—It has been shown that ethyl aminocrotonate reacts with chloroacetyl chloride to form ethyl β-amino-α-chloroacetylcrotonate (A., 1910, i, 888). It has now been found that this ester forms a hydroxythiophen derivative when treated with potassium hydrosulphide, thus:

$$NH_2\cdot CMe{:}C(CO_2Et)\cdot CO\cdot CH_2Cl + KHS \longrightarrow$$
$$NH_2\cdot CMe{:}C(CO_2Et)\cdot CO\cdot CH_2\cdot SH = S\!<\!\begin{matrix}CMe{:}C\cdot CO_2Et\\ CH{=}C\cdot OH\end{matrix} + NH_3.$$
(I.)

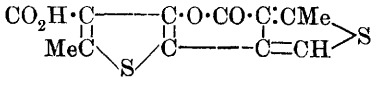
The new ester undergoes many interesting condensations because of the reactive hydrogen atom in position 2.

Ethyl β-amino-α-chloroacetylcrotonate was mixed with an aqueous-alcoholic solution of potassium or sodium hydrosulphide, when *ethyl* 3-*hydroxy*-5-*thiotolen*-4-*carboxylate* [*ethyl* 4-*hydroxy*-2-*methylthiophen*-3-*carboxylate*] (I) separated. It crystallised in white needles, m. p. 64·5—66°, gave a dark blue coloration with ferric chloride, and its solution in concentrated sulphuric acid displayed striking yellowish-green fluorescence. The *methyl* ester, from the analogous methyl crotonate (*ibid.*), had m. p. 64—65°. Hydrolysis to the acid was accomplished by shaking the ester with *N*-sodium hydroxide, saturating with carbon dioxide to precipitate any unchanged material, and then adding hydrochloric acid. 3-*Hydroxy*-5-*thiotolen*-4-*carboxylic acid*, $C_6H_6O_3S$, crystallised in yellow granules, m. p. 135°, and formed a grey *silver* salt.

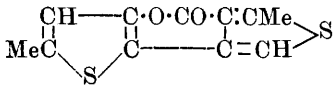
When the ester was left with concentrated hydrochloric acid, it suffered condensation to *ethyl* 3-*hydroxy*-5 : 5′-*dimethylbis*-2 : 3′-*thiophen*-4 : 4′-*dicarboxylate*, $C_{16}H_{18}O_5S_2$, which formed colourless needles, m. p. 102—103°. This ester gave a green coloration with ferric chloride and showed marked bluish-green fluorescence in sulphuric acid. It was hydrolysed to the dicarboxylic *acid* (II) by alcoholic potassium hydroxide. This decomposed at 274—276°, formed a crystalline *potassium* salt, gave similar colour reactions, and could be obtained directly by the action of concentrated hydrochloric acid on the above acid, m. p. 135°. It yielded the corresponding *lactone* (III) when boiled with hydrochloric acid, in pale brown needles, decomp. 273—275°. When this, or even the dicarboxylic acid, was distilled with lime, the *lactone* of 3-*hydroxy*-5 : 5′-*dimethylbis*-2 : 3′-*thiophen*-4-*carboxylic acid* (annexed formula) was formed, in colourless needles, m. p. 119·5°. An attempt was made to replace the hydroxyl group in the original ethyl 4-hydroxy-2-methylthiophen-4-carboxylate by bromine by means of phosphorus tribromide, but the product of the reaction was the *ethyl* ester, $C_{14}H_{12}O_4S_2$, of the lactonic acid (III). This formed soft, white needles, m. p. 158°, and could be prepared by direct esterification of the acid. It also displayed fluorescence in sulphuric acid, comparable with that of fluorescein itself.



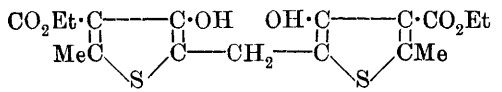
(II.)



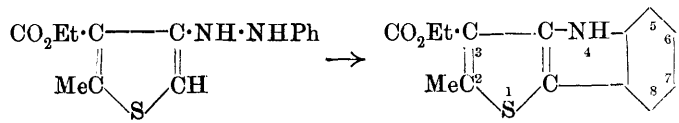
(III.)



Besides undergoing molecular condensations in the above manner, the original ester reacted with other substances. Thus, with formaldehyde and alcoholic hydrochloric acid, it yielded *ethyl* 3 : 3′-*dihydroxy*-5 : 5′-*dimethyl*-2 : 2′-*methylenebisthiophen*-4 : 4′-*dicarboxylate* (annexed formula), m. p. 115°, which formed the corresponding *acid*, m. p. 201°, on hydrolysis. This showed no tendency to give up water. Benzaldehyde yielded the analogous *ethyl* 3 : 3′-*dihydroxy*-5 : 5′-*dimethyl*-2 : 2′-*benzylidenebisthiophen*-4 : 4′-*dicarboxylate*, $C_{23}H_{24}O_6S_2$, in long needles, m. p. 121—122°, and the corresponding *acid*, m. p. 161—162°.



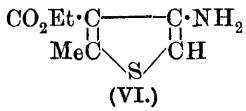
With phenylhydrazine, the ester formed the colourless 3-*phenylhydrazino*-derivative (IV), m. p. 109°, which changed into *ethyl* 2-*methyl*-*aβ*-*indolothiophen*-3-*carboxylate* (V) when warmed with acetic acid.



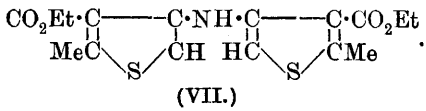
(IV.) (V.)

This formed pale yellow prisms, m. p. 171—172°, and was hydrolysed to the *acid*, decomp. 275—276°, and this was converted by distillation with lime into 2-*methyl-aβ-indolothiophen*, $\begin{matrix}CH\text{---}C\cdot NH\\ \|\quad\ \ |\\ CMe\cdot S\cdot C\cdot C_6H_4\end{matrix}$, which had m. p. 154—155°, and yielded a yellow *nitroso*-compound, m. p. 84—85°.

The original ester was also boiled, in small quantities, with solid ammonium acetate until a clear solution resulted. This was cooled, rendered alkaline, and the solid product separated by dilute hydrochloric acid into a soluble and an insoluble part. The former contained *ethyl* 4-*amino*-2-*methylthiophen*-3-*carboxylate* (VI), which crystallised in colourless leaflets, m. p. 47°, and gave a *platinichloride*, m. p. 188—189°. Like thiophenine, it formed no diazonium salt, but a brown precipitate with nitrous acid, and it seemed to couple with benzenediazonium chloride. The insoluble part consisted of *ethyl* 5 : 5′-*imino*-2 : 2′-*dimethylbisthiophen*-3 : 3′-*dicarboxylate* (VII).



(VI.)



(VII.)

This formed long, green needles, m. p. 105—106°, and the corresponding *acid* decomposed at 262—263°, and gave a crystalline *potassium* salt. When the ester (VI) was hydrolysed and the solution acidified by acetic acid, 4-*acetylamino*-2-*methylthiophen*-3-*carboxylic acid*,

$$S\begin{matrix}<CMe:C\cdot CO_2H\\ \quad CH{=}C\cdot NHAc\end{matrix},$$

separated as a very sparingly soluble substance. J. C. W.

Trithienylcarbinol. A. E. Tschitschibabin and N. N. Gavrilov (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1614—1619).—The compound obtained by the action of magnesium thienyl iodide on dithienyl ketone, which should yield trithienylcarbinol, is extremely readily soluble in even dilute acids, giving brownish-orange solutions, with an intensity of colour similar to those of solutions of dyes. When considerably diluted with water, these solutions become decolorised, but only in the absence of a marked excess of acid. The solutions, as with trithienylcarbinol itself, readily undergo change, so that the coloured salts cannot be obtained pure; the double salt of the chloride with zinc chloride has, however, been separated and analysed. Trithienylcarbinol is, therefore, a base or pseudo-base, with properties intermediate to those of triphenylcarbinol, which gives coloured solutions only in very strong acids, and those of the basic dyes, such as magenta; in the extent to which its salts are hydrolysed it resembles the latter more closely than the former. These dyes cannot possess quinonoid formulæ similar to those given by Nencki for magenta and its analogues, the only possible configurations being: (1) a para-quinonoid structure (I) such as Kehrmann's formula for triphenylchloromethane in dye solutions (II):

$$C(C_4H_3S)_2{:}C\begin{matrix}<CH:CH\\ \quad SCl:CH\end{matrix}\ (I.)\qquad CPh_2{:}C\begin{matrix}<CH:CH\\ \quad CH:CH\end{matrix}>CHCl\ (II.),$$

and (2) the carbonium formula, $C(C_4H_3S)_3Cl$. These salts evidently exhibit characters approximating to those of dyes and yet contain no typical auxochrome group.

Thienylcarboxylic acid, m. p. 125°, is obtained in good yield by the action of carbon dioxide on magnesium thienyl iodide. Dithienyl ketone, m. p. 88°, b. p. 326°, is readily prepared by the interaction of thiophen and the chloroanhydride of thienylcarboxylic acid in presence of aluminium chloride. Trithienylcarbinol was obtained as a greenish-yellow oil, which undergoes gradual conversion into an amorphous mass. The *double chloride* of trithienylcarbinol and zinc,

$$2(C_4H_3S)_3CCl,ZnCl_2,$$

forms dark orange crystals with a green, magenta-like reflection, and is extremely stable, even in aqueous solution. T. H. P.

Triarylmethyls. XIV. Theory of the "Quinocarbonium Salts." W. Schlenk and R. Ochs (*Ber.*, 1915, **48**, 676—680).—In order to support the contention that the so-called "quinocarbonium salts" are simple carbonium compounds and are not quinonoid (A., 1914, i, 823), the authors have prepared tri-2-thienylcarbinol,

$$(C_4SH_3)_3C\cdot OH,$$

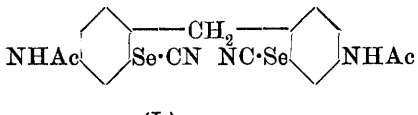
in which quinonoid structure is out of the question. Although the pure carbinol could not be isolated, a perchlorate was obtained which had all the characteristics of triphenylmethyl perchlorate, from which the conclusion is drawn that the latter is not quinonoid.

Thiophen (not more than 37 grams at a time) was diluted with benzene, mixed with fresh, powdered mercuric oxide, and then shaken with successive portions of iodine, under reflux. The filtered solution was then distilled, and 2-iodothiophen was obtained as a pale yellow oil, b. p. 78°/20 mm. This was readily converted by the Grignard method into thiophen-2-carboxylic acid, m. p. 124°, and this into the ethyl ester, b. p. 96°/18 mm. Magnesium thienyl iodide was then added to the ester, and the ethereal solution was boiled for two hours and finally decomposed by cold sulphuric acid. The dark ethereal solution of the carbinol was immediately mixed with 70% perchloric acid, when *tri-2-thienylmethyl perchlorate*, $(C_4SH_3)_3C\cdot O\cdot ClO_3$, soon separated, in shimmering blue crystals. Like triphenylmethyl perchlorate, the salt appears yellowish-brown when powdered, gives deep yellow solutions in *s*-tetrachloroethane, and exhibits the characteristic spectrum and electrical conductivity (Hofmann, A., 1910, i, 168). J. C. W.

3 : 6-Diaminoselenopyronine. [3 : 6-Diaminoxanthoselenonium.] P. Ehrlich and Hugo Bauer (*Ber.*, 1915, **48**, 502—507).—The selenium analogue of 3 : 6-diaminothiopyronine (Kehrmann and Löwy, A., 1912, i, 207) has been prepared in order to learn the influence of selenium on the colour and biological action of the substance (compare also 1 : 3-diaminophenazselenonium chloride, A., 1914, i, 871).

pp'-Diaminodiphenylmethane was nitrated in the presence of sulphuric acid, and the solution diluted to a point at which the sulphate crystallised out, this being an improvement on the existing methods (Duval, A., 1910, i 588). The diacetyl derivative (Duval)

was also obtained in quantitative yield and reduced by alcoholic stannous chloride at 40°. The *oo'*-diamino-*pp'*-diacetylaminodiphenylmethane was dissolved in hydrochloric acid, cooled, and the crystalline mass of the salt was stirred with sodium nitrite until the formation of the brown precipitate of the bisdiazo-compound was complete. The mineral acid was then neutralised by sodium acetate and the mixture stirred with potassium selenocyanate. The expected product (I) could not be purified, but it suffered condensation and hydrolysis of the acetyl groups when dissolved in concentrated sulphuric acid. The deep red solution was diluted with water, the dye dissolved again in hydrochloric acid, and reprecipitated by dilution as the *chloride* of 3 : 6-*diaminoselenopyronine* [3 : 6-*diaminoxanthoselenonium*] (II).



(I.)



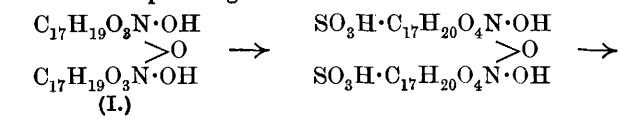
(II.)

The dye forms small needles with green, metallic lustre. The solutions are more bluish-red than those of the sulphur analogue and show no fluorescence. The substance has little value as a dye or as a drug in cases of trypanosomiasis. J. C. W.

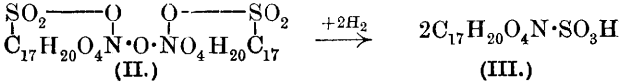
Compounds of Cinchona Alkaloids with Metals and Phosphoric Acid. EDWIN D. WATKINS (*Biochem. Bull.*, 1915, **4**, 94—95).—Compounds were obtained of silver with quinine and orthophosphoric acid; these are stated to be of therapeutic value; all attempts to crystallise the compounds failed; two crystals were found by accident in a specimen which had been kept for fifteen months. Non-crystallisable copper compounds were also obtained. W. D. H.

Morphine. MARTIN FREUND and EDMUND SPEYER [with H. HERMINGHAUS] (*Ber.*, 1915, **48**, 497—502).—A further account of morphine oxide and of the acid which it gives when treated with acetic anhydride and sulphuric acid (A., 1911, i, 76, 909).

In agreement with Mossler (codeine oxide, A., 1911, i, 223) the amine-oxide is regarded as a bimolecular compound (I). The sulphonated derivative (long needles which blacken above 280°) is named *morphinehydrateoxidesulphonic acid* (II), and the product which this gives on reduction with sulphurous acid (hard prisms, m. p. above 300°) is considered to be a *morphinehydratesulphonic acid* (III), the relationships being illustrated thus :



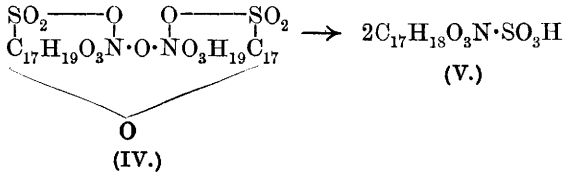
(I.)



(II.) (III.)

Full details are given of methods whereby excellent yields of these compounds can be obtained.

A further derivative has now been prepared by heating the acid (II) with concentrated sulphuric acid at 110°. It is an *anhydride* of II, having the formula IV. It crystallises in slender needles, which blacken above 250° and yield a *morphinesulphonic acid* (V), needles which blacken at 275°, when reduced by sulphurous acid.

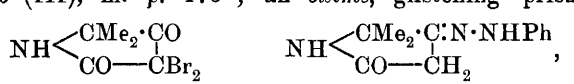


(IV.) (V.)

J. C. W.

Tetramic Acids. S. GABRIEL (*Ber.*, 1914, **47**, 3033—3039).—The author has shown that methyl phthaliminoisobutyrylmalonate is transformed into methyl carbomethoxybenzoyldimethyltetramcarboxylate when treated with sodium methoxide, a reaction shared by similar esters (A., 1913, i, 622). It was thought to be of interest to try to show the relation of such compounds to tetramic acid by direct degradation to simple derivatives of the latter. For this purpose, hydrolysis with hydrochloric acid was useless, for it led beyond the elimination of the phthalic acid and the ester residues to the opening of the ring and the formation of aminomethylbutanone, $NH_2 \cdot CMe_2 \cdot COMe$. However, the acid-esters (I.) $CO_2H \cdot C_6H_4 \cdot CO \cdot N<^{CO\text{—}CH \cdot CO_2Me \text{ (or Et)}}_{CMe_2 \cdot CO}$, have been hydrolysed to dimethyltetramic acid by the action of hot water.

Methyl phthaliminoisobutyrylmalonate (*ibid.*) was dissolved in concentrated sulphuric acid, left overnight, and then poured into water, when *methyl carboxybenzoyldimethyltetramcarboxylate* (I) separated as a soft powder, m. p. 175°, which yielded the di-ester (*ibid.*) on methylation. Ethyl phthaliminoisobutyrylmalonate gave the corresponding *ethyl* ester, m. p. 151°. They were heated with water until completely dissolved, when the product was freed from phthalic acid, and the mother liquor concentrated to a syrup and crystallised from ethyl acetate. *Dimethyltetramic acid*, $NH<^{CMe_2 \cdot CO}_{CO\text{—}CH_2}$ (compare F. de Wyl, *Diss.*, Bonn, 1913), forms prisms, m. p. 125—126·5°, gives a reddish-brown colour with ferric chloride and a dark red with potassium nitrite, and titrates as a monobasic acid. It yields a *dibromo*-derivative (II), rhombic tablets, m. p. 234—236°, insoluble in ammonia; a *phenylhydrazone* (III), m. p. 173°; an *oxime*, glistening prisms, m. p.



(II.) (III.)

205—206°; a *hydrazone*, long prisms, m. p. 200—203° (decomp.); and, at 160°, a *benzylidene* compound, yellow prisms, m. p. 168—170°.

When a warm, aqueous solution is shaken with barium carbonate and the cold filtrate is then acidified, there separates the sparingly soluble *anhydrobisdimethyltetramic acid*, $\begin{matrix}CMe_2\cdot CO\\ |\\ NH-CO\end{matrix}>C:C<\begin{matrix}CH_2-CO\\ |\\ CMe_2\cdot NH\end{matrix}$, in glistening needles, m. p. 320—321°. This behaves as a monobasic acid, and may be reduced by sodium amalgam to a similar *acid*, $C_{12}H_{18}O_3N_2$, oblong leaflets, m. p. 282—284°.

Methyl phthaliminomethylethylacetylmalonate [methyl γ-phthalimino-β-keto-γ-methyl-*n*-pentanedicarboxylate] (Pfaehler, A., 1913, i, 753) undergoes similar condensation in concentrated sulphuric acid to *methyl carboxybenzoylmethylethyltetramcarboxylate*,

$$CO_2H\cdot C_6H_4\cdot CO\cdot N<\begin{matrix}CO---CH\cdot CO_2Me\\ |\\ CMeEt\cdot CO\end{matrix},$$

which forms soft, white needles, m. p. 147—148°. J. C. W.

Action of Acylaminoacyl Chlorides on Sodiomalonic Esters. IV. E. Immendörfer (*Ber.*, 1915, **48**, 605—616).—Gabriel has shown that when trimethylhippurylmalonic [benzoylmethylamino*iso*-butyrylmalonic] esters are boiled with hydriodic acid, they are not merely hydrolysed, but even condensed to phenyltrimethylpyrrolone (A., 1913, i, 627). The author has synthesised five other hippurylmalonic esters, and finds that the condensation to a pyrrolone is a general reaction, although the yields vary.

I. *Methyl* N-*methyldiethylhippurylmalonate.*—Diethyl ketone, methylamine hydrochloride, and potassium cyanide were dissolved in water and shaken together, when *α-methylamino-α-ethylbutyronitrile*,

$$NHMe\cdot CEt_2\cdot CN,$$

was formed as an almost insoluble oil with camphor-like odour, b. p. 165—167°/765 mm.; *picrate*, long, lemon-yellow needles, decomp. 98°; *hydrochloride*, m. p. 76—77·5°. The benzoyl derivative, N-*methyldiethylhippuronitrile*, $NMeBz\cdot CEt_2\cdot CN$, crystallised in large, hexagonal plates, m. p. 112—112·5°, and was hydrolysed by solution in ice-cold, concentrated sulphuric acid to N-*methyldiethylhippuric acid* [*α-benzoylmethylamino-α-ethylbutyric acid*], $NMeBz\cdot CEt_2\cdot CO_2H$, which formed long needles, m. p. 186°. The *methyl* ester, through the chloride, had m. p. 89—91°. On boiling with concentrated hydrochloric acid, the acid was hydrolysed to *α-methylamino-α-ethylbutyric acid*,

$$NHMe\cdot CEt_2\cdot CO_2H,$$

long prisms, which sublimed on heating, the *hydrochloride* of which had m. p. 246—247°. The hippuryl chloride was prepared by means of thionyl chloride and mixed with methyl malonate, benzene, and methyl sodiomalonate. Next day the mass was diluted and carefully acidified, when *methyl* N-*methyldiethylhippurylmalonate* [*methyl* γ-*benzoylmethylamino-β-keto-γ-ethylpentanedicarboxylate*],

$$NMeBz\cdot CEt_2\cdot CO\cdot CH(CO_2Me)_2,$$

separated. This formed granules, m. p. 106—108°, and yielded 5-*phenyl*-1-*methyl*-2 : 2-*diethylpyrrolone*, $MeN<\begin{matrix}CPh=CH\\ |\\ CEt_2\cdot CO\end{matrix}$, when gradually heated to boiling in hydriodic acid. This separated as a sparingly soluble hydriodide, the filtrate containing α-methylamino-α-ethyl-

butyric acid. The free base formed leaflets, m. p. 138°; the *picrate* had m. p. 152°.

II. *Methyl* N-*methylmethylethylhippurylmalonate.* — *α-Methylamino-α-methylbutyronitrile*, NHMe·CMeEt·CN, prepared as above from methyl ethyl ketone, had b. p. 149—154°/759 mm., and formed a *picrate*, m. p. 88—89° (decomp.), and a golden-brown *platinichloride*, which blackened at 235°. The *benzoyl* derivative, $C_{13}H_{16}ON_2$, had m. p. 81—82°, and N-*methylmethylethylhippuric acid* [*α-benzoylmethylamino-α-methylbutyric acid*], NMeBz·CMeEt·CO_2H, had m. p. 164—165°, and yielded a *methyl* ester, in jagged leaflets, m. p. 85—87°. The product of hydrolysis of the acid, namely, *α-methylamino-α-methylbutyric acid*, NHMe·CMeEt·CO_2H, formed prisms which sublimed on heating, and gave a *hydrochloride*, in stout prisms, m. p. 203—204° (decomp.). *Methyl* N-*methylmethylethylhippurylmalonate* [*methyl γ-benzoylmethylamino-β-keto-γ-methylpentanedicarboxylate*],

NMeBz·CMeEt·CO·CH(CO_2Me)$_2$,

crystallised in rhombic plates, m. p. 116—118°, and yielded 5-*phenyl*-1 : 2-*dimethyl*-2-*ethylpyrrolone*, MeN$<^{\text{CPh=CH}}_{\text{CMeEt·CO}}$, m. p. 91·5—93°, when heated with hydriodic acid. The *hydriodide*, *picrate* and *aurichloride* were found to be sparingly soluble.

III. *Methyl* N-*ethyldimethylhippurylmalonate.*—Ethylamine hydrochloride, acetone, and potassium cyanide were condensed to *α-ethylamino*isobutyronitrile, NHEt·CMe_2·CN, which had b. p. 143—144°/761 mm., and formed a hygroscopic *hydrochloride*, prisms, m. p. 109—110·5°, a *picrate*, sharp needles, m. p. 166—168°, a *platinichloride*, hexagonal plates, and a soluble *aurichloride*, jagged needles. The benzoyl derivative, N-*ethyldimethylhippuronitrile*,

NEtBz·CMe_2·CN,

crystallised in large, rhombic plates, m. p. 76—78°, b. p. 275°, and N-*ethyldimethylhippuric acid* [*α-benzoylethylamino*isobutyric *acid*] formed quadratic prisms and plates, m. p. 161·5—162°, and yielded a *methyl* ester, m. p. 68°. The product of the hydrolysis of the acid by boiling hydrochloric acid, namely, *α-ethylamino*isobutyric *acid*, NHEt·CMe_2·CO_2H, formed long prisms, and gave a *hydrochloride*, m. p. 249—251° (decomp.). *Methyl* N-*ethyldimethylhippurylmalonate* [*methyl γ-benzoylethylamino-β-keto-γ-methylbutanedicarboxylate*],

NEtBz·CMe_2·CO·CH(CO_2Me)$_2$,

had m. p. 111—113°, and yielded 5-*phenyl*-2 : 2-*dimethyl*-1-*ethylpyrrolone*, EtN$<^{\text{CPh=CH}}_{\text{CMe}_2\text{·CO}}$, in quadratic prisms, m. p. 50°; *hydriodide*, m. p. 170°, *picrate*, slender needles, m. p. 145—146°.

IV. and V. *Methyl* p(m)-N-gem.-*tetramethylhippurylmalonate.* *p*-Toluoyl chloride was condensed with α-methylamino*iso*butyronitrile (Gabriel, *Ber.*, 1914, **47**, 2923) to form *α*-p-*toluoylmethylamino*isobutyronitrile, C_6H_4Me·CO·NMe·CMe_2·CN, m. p. 133°, and this was hydrolysed to the corresponding *acid*, rhombic plates, m. p. 205°. The chloride of this yielded with methyl sodiomalonate, *methyl* p-N-gem.-*tetramethylhippurylmalonate* [*methyl γ-p-toluoylmethylamino-β-keto-γ-methylbutanedicarboxylate*], C_6H_4Me·CO·NMe·CMe_2·CO·CH(CO_2Me)$_2$, in pale yellow

plates, m. p. 98—103°, which gave rise to 5-p-*tolyl*-1 : 2 : 2-*trimethylpyrrolone*, $MeN<\begin{matrix}C(C_6H_4Me):CH\\ CMe_2\text{———}CO\end{matrix}$, a base which crystallised in plates, m. p. 125°, and formed a *picrate*, m. p. 134·5—136°.

The corresponding derivatives obtained from *m*-toluoyl chloride were as follows. α-m-*Toluoylmethylaminoisobutyronitrile*, plates, m. p. 86°, the *acid*, $C_6H_4Me\cdot CO\cdot NMe\cdot CMe_2\cdot CO_2H$, m. p. 169°, *methyl* γ-m-*toluoylmethylamino-β-keto-γ-methylbutanedicarboxylate*, long needles, m. p. 112—114°, and 5-m-*tolyl*-1 : 2 : 2-*trimethylpyrrolone*, thin flakes, m. p. 83°, *picrate*, m. p. 154°.

Gabriel showed (A., 1913, i, 625) that when methyl sodiophthaliminoisobutyrylmalonate was methylated by methyl iodide and the product was hydrolysed, the ketone, $NH_2\cdot CMe_2\cdot CO\cdot CH_2\cdot CH_3$, was obtained. The author has now attempted to prepare the next homologue of this by using ethyl iodide. He found, however, that the product of the action of ethyl iodide on methyl sodiophthaliminoisobutyrylmalonate in acetone was ethyl benzoylenedimethylpyrrolonecarboxylate (A., 1911, i, 218). The reaction was therefore examined, and it was found that the sodium compound quickly changes on boiling with water, slowly with ethyl iodide or acetone, into the ring compound. Methyl iodide reacts so readily in the normal way that the ring-formation is prevented. J. C. W.

4-Hydroxy- and 4-Amino-piperidine. Bruno Emmert and Wilhelm Dorn (*Ber.*, 1915, **48**, 687—692).—Although many alkaloids contain the 4-hydroxypiperidine system, the base itself was hitherto unknown. It has now been obtained from 4-hydroxypyridine by reduction with sodium and alcohol, the electrical method which succeeded in the case of the corresponding 2 : 6-dicarboxylic acid (A., 1912, i, 382) being unsuitable in this case.

Chelidamic acid was introduced in portions of about 20 grams at a time into a flask at 230—250°, and the resulting 4-hydroxypyridine was subsequently distilled under reduced pressure. This base was dissolved in alcohol, and sodium was added at such a rate that a good reflux condenser could just control the boiling. The product, *4-hydroxypiperidine*, $C_5H_{11}ON$, had b. p. 211—212° (corr.)/745 mm., m. p. 86°. It readily absorbed carbon dioxide, gave precipitates with the alkaloid reagents, and the hygroscopic *hydrochloride* and *aurichloride* formed long prisms. The *benzoyl* derivative [*4-piperidyl benzoate*],

$$C_5NH_{10}\cdot OBz,$$

was obtained as a colourless liquid, b. p. 169—170°/12 mm., which formed a *hydrochloride*, m. p. 230°, an *aurichloride*, needles, a *platinichloride*, short prisms, and a *nitroso*-derivative,

$$NO\cdot C_5NH_9\cdot OBz,$$

as a white substance, m. p. 77—79°.

4-Aminopyridine was conveniently prepared by heating 4-chloropyridine with fresh zinc ammonium chloride at 220—230° in sealed tubes, and was also reduced by sodium and alcohol. The alcoholic solution was diluted with an equal volume of water and evaporated to about one-third, the distillate containing ammonia and piperidine, and then the remainder was distilled until the flask fused. This distillate was

evaporated with hydrochloric acid, and the *hydrochloride* of 4-*aminopiperidine*, $C_5H_{14}N_2Cl_2$, was finally obtained in crystals, m. p. 332—335°; *platinichloride*, stout prisms. The free base could not be completely dried. J. C. W.

Compounds of Iridium Chloride with Organic Bases. A. GUTBIER [with D. HOYERMANN] (*Zeitsch. anorg. Chem.*, 1914, **89**, 340—343. Compare Renz, A., 1903, i, 774).—Iridium chloride, pyridine, and hydrochloric acid react to form a yellow salt, pyridinium iridichloride, $(C_5NH_6)_2IrCl_6$, whilst pyridine and an alcoholic solution of iridium chloride yield the additive compound, $(C_5NH_5)_2IrCl_4$. Quinoline similarly forms $(C_9NH_7)_2IrCl_4$. The compounds $(C_5NH_4Me)_2IrCl_4$ and $(C_5NH_5Me)_2IrCl_6$ are obtained in similar manner from α-picoline. C. H. D.

Polymerism of Pyridinecarboxyl Chlorides. HANS MEYER and HANS TROPSCH (*Monatsh.*, 1914, **35**, 781—786).—According to Meyer, the sparing solubility, high m. p., and slight reactivity of the pyridinecarboxyl chlorides point to the latter substances being polymerides of high molecular weight. The chlorides of the pyridinedicarboxylic acids, on the other hand, are characterised by their low m. p. and ready solubility, and, therefore, are considered to represent monomolecular modifications. The authors now record the existence of pyridine-3 : 5-dicarboxyl chloride in two forms which are readily converted into one another, a readily fusible monomolecular modification and a less fusible polymeride.

Pyridine-3 : 5-*dicarboxyl chloride* is obtained in the form of its *hydrochloride* by heating the corresponding acid for several hours with thionyl chloride. The hydrochloride forms small, lustrous, colourless crystals, m. p. 110—115°, and when heated in benzene solution loses hydrogen chloride with the formation of the monomolecular chloride, which crystallises in long needles, m. p. 66°, and is readily soluble in indifferent organic media. When kept the monomolecular chloride is transformed into an insoluble polymeride, which does not fuse below 280°. The velocity of polymerisation depends on conditions which cannot be defined, some preparations of the chloride undergoing almost complete polymerisation during the course of a few hours, whilst others may be kept for weeks without undergoing appreciable change. Both chlorides yield the same methyl ester and *amide*, small needles, m. p. 303—304° (decomp.).

The existence of ethyl lutidinate in dimorphous forms is also recorded. The ester crystallises from light petroleum in long, lustrous needles, m. p. 56—57°, which slowly disintegrate when kept and then have m. p. 60—61°. The new modification is transformed by fusion or crystallisation from light petroleum into the more fusible form. F. B.

Behaviour of βγ-Unsaturated Cyclic Bases towards Cyanogen Bromide. J. VON BRAUN and E. AUST (*Ber.*, 1914, **47**, 3023—3027).—Braun has shown that cyclic, *N*-methylated bases suffer

rupture of the ring when treated with cyanogen bromide provided that there is an ethylene linking in the $\beta\gamma$-position relatively to the nitrogen atom, or loss of the methyl group if the base is saturated, and he has applied these facts to the question of the constitution of morphine (A., 1914, i, 1138).

In order to test the facts with more complicated bases of definite structure than those originally used, the Grignard reagent has been applied to quinoline methiodide (compare Freund, A., 1905, i, 156; 1909, i, 417) to give dihydroquinolines, and these, by reduction, tetrahydroquinolines,

$$C_6H_4\begin{cases}CH{=}CH\\ NMe{\cdot}CHR\end{cases} \quad \text{and} \quad C_6H_4\begin{cases}CH_2{-}CH_2\\ NMe{\cdot}CHR\end{cases}.$$

These behave exactly in the expected way towards cyanogen bromide.

Quinoline methiodide and magnesium propyl iodide yielded *1-methyl-2-propyldihydroquinoline*, $C_{13}H_{17}N$, as a pale yellow, mobile, unstable oil, b. p. 168—170°/21 mm. The reaction with cyanogen bromide was very violent except when much ether was used as a diluent, when a dark, insoluble compound, probably

$$CN{\cdot}NMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CHBr{\cdot}C_3H_7,$$

was obtained. It could not be purified. The base was reduced by tin and hydrochloric acid to the stable *1-methyl-2-propyltetrahydroquinoline*, $C_{13}H_{19}N$, b. p. 151—157°/20 mm., *picrate*, stout prisms, m. p. 120°. This reacted quietly with cyanogen bromide to give a 75% yield of *1-cyano-2-propyltetrahydroquinoline*, $C_{13}H_{16}N_2$, as a pale yellow oil, b. p. 201—202°/20 mm., which was heated with concentrated hydrochloric acid at 110° and converted into *2-propyltetrahydroquinoline*, $C_{12}H_{17}N$. This has b. p. 152°/20 mm., forms a very characteristic, sparingly soluble *hydrochloride*, m. p. 220°, a *benzoyl* derivative, plates, m. p. 97°, and a *picrate*, long needles, m. p. 143°. It may or may not be identical with the "α-propyltetrahydroquinoline" mentioned in "Beilstein." At any rate, this seems to be the best way to obtain such compounds. J. C. W.

Quinoneimide Dyes. IV. The Spectra of the Simplest Thiazine Dyes. F. Kehrmann, J. Speitel, and E. Grandmougin [with G. Diserens] (*Ber.*, 1914, **47**, 2976—2983).—The view was originally held that phenazothionium only formed monacid salts, and that these were *holo*-quinonoid (A., 1914, i, 868, 971). The first unmistakably *holo*-quinonoid salt was, however, the perchlorate which Pummerer and Gassner (A., 1913, i, 991) obtained from thiodiphenylamine sulphoxide (Smiles and Barnett, T., 1909, **95**, 1261). The ordinary salts are, therefore, *meri*-quinonoid, and phenazothionium in reality forms two series of salts, like the azoniums. 3 : 6-Dimethylphenazothionium also gives two series of salts, and it is recognised that the reason why 3-aminophenazothionium was said to form only two series of salts instead of three is that the colour of the tri-acid salts is hardly distinguishable to the eye from that of the di-acid salts. The existence of three series of salts in the case of the 1-amine is not proved, however, for only the chloride is known in the solid state, and this, despite all precaution, becomes *meri*-quinonoid in concentrated sulphuric acid.

It is expected that the azoxoniums will also prove to be normal and form two series of salts.

When a few drops of concentrated sulphuric acid containing hydrogen peroxide are added to the greenish-orange solutions obtained by the oxidation of thiodiphenylamine by concentrated sulphuric acid, the colour changes to the green exhibited by a solution of pure thiodiphenylamine sulphoxide in the same acid. The phenazothionium sulphate is, therefore, a *meri*-quinonoid salt, although it may seem strange that the vigorous action of concentrated sulphuric acid should stop at this stage. This is all the more remarkable since 3 : 6-dimethylthiodiphenylamine behaves differently. It dissolves in cold, concentrated sulphuric acid to give the magenta-coloured *meri*-quinonoid salt, but this is soon oxidised further, by the air, to the brownish-red *holo*-quinonoid salt. On diluting these *holo*-quinonoid di-acid salt solutions, the *meri*-quinonoid monacid salts are developed, but the *holo*-quinonoid salts are stable in glacial acetic acid. The changes were followed by the spectrographic method.

The 3-amino-derivative gives violet monacid salts in dilute acids, pure green di-acid salts in 60% sulphuric acid, both series being para-quinonoid, and somewhat yellowish-green tri-acid, ortho-quinonoid salts in the concentrated acid. The di-acid salts show absorption bands at λ 454, 435 and 300 $\mu\mu$, and the tri-acid salts at the extreme red and 460 $\mu\mu$, that is, the same as the *holo*-quinonoid phenazothionium disulphate. J. C. W.

Alkylated *p*-Phenylenediamines and Derivatives. Quinoneimide Ammonium Compounds. Raphael Meldola and William Francis Hollely (T., 1915, **107**, 610—622).—The work described in this paper was undertaken with the object of preparing compounds of the true quinoneimide-ammonium type, $NH{:}C_6H_4{:}N.abc$., and especially those in which *a*, *b*, and *c* are represented by different radicles. An investigation of the dialkylphenylenediamines required for such experiments has shown that the acetyl derivatives of these compounds all yield 3 : 5-dinitro-1-acetylaminophenyl-4-methylnitrosoamine on nitration.

Methylethylacetyl-p-*phenylenediamine* (p-*methylethylaminoacetanilide*), $NHAc{\cdot}C_6H_4{\cdot}NMeEt$, m. p. 92°, obtained by reducing nitrosomethylethylaniline with tin and hydrochloric acid and acetylating the resulting methylethyl-*p*-phenylenediamine hydrochloride, crystallises in colourless, silky needles. It readily combines with alkyl iodides, except *iso*propyl iodide, with formation of quaternary ammonium iodides, which yield beautiful crystals, are soluble in water, and when decomposed with moist silver oxide furnish syrupy bases which readily absorb carbon dioxide from the air. *Methylethylpropyl*- and *methylethylallyl*-4-*acetylaminophenylammonium iodides* could doubtless be resolved into optically active isomerides, but this has not yet been accomplished. The acetyl group can be readily removed by hydrolysis with formation of aminophenylammonium compounds, which may prove of service for the synthesis of quinone-ammonium derivatives containing an asymmetric nitrogen atom. When methylethylpropyl-4-acetylaminophenyl-

ammonium iodide is submitted to repeated evaporation with concentrated hydrobromic acid, it yields a *dibromide*,

$$HBr,NH_2\cdot C_6H_4\cdot NMeEt(C_3H_7)Br,$$

which crystallises in colourless tablets.

3 : 5-*Dinitro*-1-*acetylaminophenyl*-4-*methylnitrosoamine*,

$$NHAc\cdot C_6H_2(NO_2)_2\cdot NMe\cdot NO,$$

m. p. 152—153°, obtained by the nitration of dimethyl-, methylethyl-, or benzylmethyl-acetyl-*p*-phenylenediamine, forms colourless crystals, and when boiled with phenol is converted into 3 : 5-*dinitromethylacetyl*-p-*phenylenediamine*, $NHAc\cdot C_6H_2(NO_2)_2\cdot NHMe$, m. p. 196—197°, which crystallises in small, scarlet needles. When the dinitronitrosoamine is dissolved in fuming nitric acid at 0°, the corresponding *nitroamine*, $NHAc\cdot C_6H_2(NO_2)_2\cdot NMe\cdot NO_2$, m. p. 183—184°, is produced, which forms tufts of white needles; it is converted by boiling phenol into 3 : 5-dinitromethylacetyl-*p*-phenylenediamine and by concentrated sulphuric acid into the original nitrosoamine. 3 : 5-*Dinitromethyl*-p-*phenylenediamine*, $NH_2\cdot C_6H_2(NO_2)_2\cdot NHMe$, m. p. 186—187°, obtained by heating its acetyl derivative with concentrated sulphuric acid, crystallises in dark purple needles with a green lustre. When 3 : 5-dinitro-*p*-acetylaminophenyl-4-methylnitrosoamine is boiled with alcoholic hydrochloric acid, 2 : 6-dinitromethylaniline is produced, which reacts with nitrous acid to form 2 : 6-*dinitrophenyl*-1-*methylnitrosoamine*, m. p. 115—116°, which crystallises in white needles.

Dimethylacetyl-*p*-phenylenediamine (dimethylamino-*p*-acetanilide) has m. p. 132—133°; its *picrate*, m. p. 206—208°, and *ferrocyanide* are described. By the action of nitrous acid on this compound, a *substance*, m. p. 132—133°, is obtained, which forms short, red prisms, and does not seem to be a nitrosoamine.

Benzylmethyl-p-*nitroaniline*, m. p. 68—69°, obtained by the action of methyl sulphate on benzyl-*p*-nitroaniline, forms yellow, silky needles. On reduction with tin and hydrochloric acid, it yields *benzylmethyl*-p-*phenylenediamine*, $NH_2\cdot C_6H_4\cdot NMe\cdot C_7H_7$, which furnishes a *hydrochloride*, crystallising in white needles, and a *ditoluenesulphonyl* derivative, $C_7H_7\cdot NMe\cdot C_6H_4\cdot N(SO_2\cdot C_6H_4Me)_2$, m. p. 217°, which forms colourless scales. The *acetyl* derivative,

$$NHAc\cdot C_6H_4\cdot NMe\cdot C_7H_7,$$

m. p. 110—111°, crystallises in white, silky needles, and does not combine with alkyl iodides.

When dimethylacetyl-*p*-phenylenediamine methiodide is treated with silver nitrate, it is converted into the *trimethylammonium nitrate*,

$$NHAc\cdot C_6H_4\cdot NMe_3\cdot NO_3,$$

which forms flat, colourless needles. This compound on nitration yields 2 : 3 : 5-*trinitro*-4-*trimethylammonium*-1-*benzoquinoneimide*,

$$NH{:}C_6H(NO_2)_3{:}NMe_3 \text{ or } C_6H(NO_2)_3\langle\begin{matrix}NH\\ |\\ NMe_3\end{matrix},$$

which crystallises in golden yellow scales and decomposes at 200—220°. The solution of the hydrochloride of the quinoneimide is colourless, and on neutralising it with alkali, crystals of the yellow quinoneimide separate. The quinoneimide is unstable, and definite derivatives have not yet been obtained. On heating the acid solution to near the b. p.,

decomposition takes place with evolution of gas and formation of a crystalline substance which is volatile in steam and has not been identified. E. G.

Some Hydrazine Derivatives. S. GABRIEL (*Ber.*, 1914, **47**, 3028—3033).—Attempts have been made to prepare halogenated hydrazines by the addition of halogen hydrides to unsaturated hydrazines and by the scission of phenoxyhydrazines, methods which have proved successful in the case of the amines. Some phenoxyhydrazines are now described, but their scission has not yet been accomplished.

Phenoxyethylamine hydrochloride (Schmidt, A., 1890, 373) was evaporated with potassium cyanate, and the resulting *β-phenoxyethylcarbamide*, $OPh\cdot C_2H_4\cdot NH\cdot CO\cdot NH_2$, long, white needles, m. p. 120—121°, was converted by nitrous fumes in ether into the *nitroso*-derivative, $OPh\cdot C_2H_4\cdot N(NO)\cdot CO\cdot NH_2$, pale yellow, quadratic leaflets, m. p. 103°, and this was reduced by zinc dust and acetic acid to *β-phenoxyethylsemicarbazide*, $OPh\cdot C_2H_4\cdot N(NH_2)\cdot CO\cdot NH_2$, needles, m. p. 119—119·5°. The latter should give the hydrazine on hydrolysis, but a much better way to obtain this is by boiling an alcoholic solution of *β*-bromophenetole (from dry sodium phenoxide and ethylene dibromide) with hydrazine hydrate. *β-Phenoxyethylhydrazine*,

$$OPh\cdot C_2H_4\cdot NH\cdot NH_2,$$

is a strongly alkaline base, b. p. 279—281°, which forms a hygroscopic *hydrochloride*, a *picrate*, cubes or oblong columns, m. p. 130·5—132° (decomp.), a *benzylidene* compound, $OPh\cdot C_2H_4\cdot NH\cdot N{:}CHPh$, leaflets, m. p. 77·5—79°, and a *phthalyl* derivative, $C_{16}H_{14}O_3N_2$, pale yellow leaflets, m. p. 177—179°.

γ-Phenoxypropylhydrazine was obtained as a *hydrochloride*,

$$OPh\cdot[CH_2]_3\cdot NH\cdot NH_2,HCl,$$

m. p. 120—125°, in the same way, from phenyl γ-chloropropyl ether. Similarly, allyl chloride and hydrazine hydrate yielded *allylhydrazine*, $CH_2{:}CH\cdot CH_2\cdot NH\cdot NH_2$, as a very hygroscopic, strongly alkaline base, b. p. 122—124°/757·5 mm., which forms a *dihydrochloride*, m. p. 140°. In the usual way the base was converted into *phenylallylthiosemicarbazide*, $C_3H_5\cdot NH\cdot NH\cdot CS\cdot NHPh$, glistening, rhombic prisms, m. p. 122—123°, and into *allylthiosemicarbazide*, $C_3H_5\cdot NH\cdot NH\cdot CS\cdot NH_2$, bundles of needles, m. p. 123·5—124·5°, but it could not be made to take up the elements of hydrogen bromide at the ethylene linking.

Ethylene oxide was added to a cold mixture of hydrazine hydrate and methyl alcohol, then left for three days in a sealed tube, and finally warmed for a few hours at 100°. In this way, *β-hydroxyethylhydrazine*, $OH\cdot CH_2\cdot CH_2\cdot N_2H_3$, was obtained as a colourless, viscous base, b. p. 218—220°/754 mm., which forms a *dihydrobromide*, hard, white, hygroscopic crystals, m. p. 151—152°, and a *picrate*, lemon-yellow needles, m. p. 123°. J. C. W.

Product of the Action of Ethyl Oxalate on 1 : 2-Diaminoanthraquinone. ARTHUR ERTL (*Monatsh.*, 1914, **35**, 1427—1430).—The substance, m. p. 276—277°, obtained by Terres (A., 1913, i, 737) by evaporating a solution of equal parts of ethyl oxalate and 1 : 2-diaminoanthraquinone in glacial acetic acid to half its bulk and

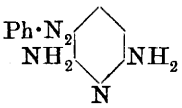
described by him as 2 : 3-diethoxypyrazinoanthraquinone, consists of a mixture of $\alpha\beta$-dihydroxy-1 : 2-pyrazinoanthraquinone, unchanged diaminoanthraquinone, and possibly other products. $\alpha\beta$-Dihydroxy-1 : 2-pyrazinoanthraquinone may be prepared in pure condition by the prolonged heating of diaminoanthraquinone with a large excess of ethyl oxalate in glacial acetic acid solution. It begins to sublime at 300°, chars without melting at 370°, and is identical with the compound obtained by Scholl and Edlbacher (A., 1911, i, 756) by the oxidation of indanthren with chromic acid. F. B.

New Reaction of Compounds containing the Pyridine Nucleus. A. E. Tschitschibabin and O. A. Zeide (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1216—1236).—The action of sodamide on pyridine at a temperature not exceeding 120° and subsequent decomposition of the product with water yields 2-aminopyridine in 70% yield: $C_5H_5N + NH_2Na = C_5H_4N\cdot NHNa + H_2$ and

$$C_5H_4N\cdot NHNa + H_2O = C_5H_4N\cdot NH_2 + NaOH.$$

Sodamide does not react with 2 : 4 : 6-trimethylpyridine under the above conditions. As regards the possible formation of 4-amino-derivatives of pyridine by this method, a very small proportion of a compound having the external appearance and the melting point of 4-aminopyridine is obtained from the products of the interaction of sodamide and pyridine, but this question requires further investigation. The study of the action of sodamide on 2-methylquinoline is also incomplete, owing to the difficulty of obtaining the pure methylquinoline. With methyl iodide and 2-methylpyridine, sodamide yields principally 6-dimethylamino-2-methylpyridine.

The action of sodamide on pyridine may proceed still further, both α-hydrogen atoms being replaced with formation of 2 : 6-diaminopyridine, which is obtained in good yield and serves as the initial product for the preparation of a whole series of new derivatives of pyridine. The most important property of 2 : 6-diaminopyridine is that it may be coupled with diazo-compounds, such as that of *m*-phenylenediamine, giving true azo-dyes, the simplest of which possesses the annexed structure; reduction of this should yield 2 : 5 : 6-triaminopyridine.



Besides amino-derivatives, the action of sodamide on pyridine and quinoline bases yields various secondary products. Some of these appear to be products of the polymerisation of pyridine and quinoline, such as dipyridines and diquinolines, whilst others are aminodipyridines and possibly aminodipyridyls, formed by the action of sodamide on these polymerised products; the secondary products formed increase in amount as the temperature of the reaction is raised.

Pyridine and sodanilide interact, but the yield of anilinopyridine obtained is very small.

Marckwald (A., 1893, i, 727; 1894, i, 381) showed that the action of sodium nitrite on a solution of 2-aminopyridine in fuming hydrochloric acid yields 2-chloropyridine in good yield. In a similar manner, although in poor yield, 2-bromopyridine and 2-fluoropyridine, a liquid

with a sweetish taste, b. p. 129°, may be obtained. 2-Aminopyridine may be readily nitrated, thus differing from pyridine and resembling aniline.

The reaction of pyridine derivatives with sodamide proceeds best in presence of a solvent neutral to sodamide, such as toluene, xylene or, in cases where a higher temperature is required, dried vaselin oil. The latter and certain other solvents, particularly dimethylaniline, facilitate the reaction, owing to the fact that the sodium derivatives of amines are soluble in them, the reaction thus proceeding in a homogeneous medium. Access of atmospheric oxygen must be prevented during the reaction. Water is subsequently added gradually to the cooled products, which are kept well mixed and cooled.

The action of sodamide and methyl iodide on 2-methylpyridine yields: (1) 6-*dimethylamino*-2-*methylpyridine*, $C_8H_{12}N_2$, which is a colourless liquid, b. p. 198—200°, with a marked, basic odour, and may also be obtained by heating 6-amino-2-pyridine with water, magnesium oxide, and methyl iodide in a sealed tube; its *platinichloride*, $(C_8H_{12}N_2),H_2PtCl_6$, m. p. 190° (decomp.), and its *picrate*, $C_8H_{12}N_2,C_6H_3O_7N_3$, m. p. 153°, were prepared; (2) 6-amino-2-methylpyridine.

The action of sodamide and methyl iodide on pyridine yields: (1) 2-*dimethylaminopyridine*, $C_7H_{10}N_2$, b. p. 196°, which gives a *picrate*, m. p. 182°; (2) a base, which from the composition of its picrate, $C_6H_8N_2,C_6H_3O_7N_3$, m. p. 190°, appears to be a monomethylaminopyridine.

With quinoline, sodamide gives 2-aminoquinoline in 25% yield, together with a large fraction, b. p. above 250°/20 mm., which is under investigation.

The properties of the 2 : 6-diaminopyridine obtained by the interaction of pyridine and sodamide in vaselin oil at 125—180° are in agreement with those given by Meyer and Tropsch (A., 1914, i, 439), with the exception of the melting point, which is found to be 122°.

Di-2-*pyridylamine*, $C_{10}H_9N_3$, obtained by heating 2-chloropyridine and 2-aminopyridine with fused zinc chloride in a sealed tube at 200°, crystallises in long, colourless needles, m. p. 86—87°; its solution in concentrated sulphuric acid gives no coloration with nitric acid.

T. H. P.

Nitration of 2-Aminopyridine. A. E. Tschitschibabin (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1236—1244).—After unsuccessful attempts by many investigators to nitrate pyridine, Friedl (A., 1912, i, 299; 1913, i, 754) has succeeded, by very vigorous nitration, in obtaining a small yield of 3-nitropyridine. Marckwald (A., 1894, i, 381) showed that the presence of an amino-group in the molecule of a pyridine compound greatly facilitates nitration, and the author finds that 2-aminopyridine (compare preceding abstract) undergoes nitration with approximately the same ease as aniline. The principal product is 5-nitro-2-aminopyridine, this being accompanied by a considerably lower proportion of an isomeride which, from the results obtained in the nitration of pyridine and of aniline, is regarded as 3-nitro-2-aminopyridine; no other nitro-derivative is formed in appreciable quantity. The

nitroaminopyridines bear a certain resemblance to the nitroanilines, being yellow compounds and exhibiting the properties of feeble bases, the salts of which are readily decomposed by water. Like *p*-nitroaniline, 5-nitro-2-aminopyridine is distilled only with difficulty in a current of steam, whereas 3-nitro-2-aminopyridine resembles *o*-nitroaniline in being readily volatile under these conditions. On the other hand, the behaviour of 5-nitro-2-aminopyridine is analogous, not to that of *p*-nitroaniline, but to that of 2-aminopyridine; in concentrated sulphuric acid, this action yields nitrogen and 5-nitro-2-hydroxypyridine. The formation of a diazo-compound is not revealed by means of phenols or amines, but diazotisation in concentrated hydrochloric acid results in replacement of the amino-group by a chlorine atom, with formation of 2-chloro-5-nitropyridine. Meyer and Staffen's statement (A., 1913, i, 530) that 2 : 5-diaminopyridine, which is obtainable also by reduction of 5-nitro-2-aminopyridine, does not exhibit the ordinary reaction of *p*-phenylenediamine, is not quite accurate. Thus, although 2 : 5-diaminopyridine does not appear to react with ferric chloride in presence of hydrogen sulphide in the cold, a dark blue, flocculent precipitate, turning green with concentrated sulphuric acid, is obtained on heating.

5-*Nitro*-2-*aminopyridine*, $C_5H_5O_2N_3$, forms yellow plates, m. p. 188°, and dissolves in mineral acids, giving colourless salts, but these solutions turn yellow on dilution with water owing to the liberation of the base.

5-*Nitro*-2-*hydroxypyridine*, $C_5H_4O_3N_2$, which is also obtained when the mixed products from the nitration of 2-aminopyridine are left overnight, forms faintly yellow needles, m. p. 184°, and exhibits feeble basic, but marked phenolic properties. With concentrated alkali hydroxide it yields yellow needles of the alkyl phenoxide, which is readily soluble in cold water.

2-*Chloro*-5-*nitropyridine*, $C_5H_3O_2N_2Cl$, forms coarse needles, m. p. 108—110°.

3-*Nitro*-2-*aminopyridine* (?), $C_5H_5O_2N_3$, forms yellow needles, m. p. 162°, and is readily volatile at 100°. T. H. P.

The Transformation of Antipyrine into Diantipyrylmethane by Formaldehyde. Ch. Astre (*Bull. Soc. chim.*, 1915, [iv], **17**, 175—179).—The method described in the Codex for estimating antipyrine in the presence of pyramidone by heating with formaldehyde and hydrochloric acid, is inaccurate, since the pyramidone, being insoluble in concentrated solutions of ammonium chloride, crystallises out when the mixture is saturated with ammonia. The amount of diantipyrylmethane obtained also depends on the time of heating and the concentration of the acid, diminishing as the concentration of the acid increases and as the heating is prolonged. In the absence of pyramidone, acid is not necessary for the conversion of antipyrine into diantipyrylmethane by formaldehyde, this taking place quantitatively in water alone in a platinum vessel, or a glass vessel previously washed with acid. A trace of alkali retards the reaction and makes it incomplete, and in this respect pyramidone is much more effective than mineral alkalis, and entirely prevents the transformation, unless sufficient acid is added just to neutralise the pyramidone. W. G.

Hydroxyl Derivatives of Indigotin. P. FRIEDLÄNDER and O. SCHENCK (*Ber.*, 1914, **47**, 3040—3052).—Hydroxyindigotins have been synthesised from hydroxy-*o*-nitrobenzaldehydes by the acetone and alkali method. The only definite simple aldehyde of this type would not yield a dye under any conditions, although the methoxy-derivative will do so. It was therefore thought that the chlorohydroxy-*o*-nitrobenzaldehydes would be more suitable, as chlorine usually confers stability on indigotins. This was the case, for the *o*-nitro-derivatives of 2-chloro- and 2 : 4-dichloro-5-hydroxybenzaldehydes readily yield indigotins.

When these were examined, it was found that the hydroxyl group had rendered the compounds sensitive towards alkalis, which explained the failure to obtain indigotins from the non-chlorinated *o*-nitrohydroxybenzaldehyde. It was expected, therefore, that esters of these would give indigotins which could be subsequently hydrolysed again. The carbonyl, acetyl, and benzoyl derivatives, however, were so readily hydrolysed that this happened before the formation of indigotins could set in. The *p*-toluenesulphonates and diphenylcarbamates, on the other hand, gave indigotins readily enough, but these were remarkably resistent to hydrolysis by acids or cold alkalis. Prolonged action of alkalis being out of the question, the esters were reduced to the indigo-whites and these could then be hydrolysed safely and re-oxidised.

The nitro-*m*-hydroxybenzaldehydes have been carefully examined, and a new one, 2-nitro-3-hydroxybenzaldehyde, characterised by many derivatives.

m-Hydroxybenzaldehyde was nitrated by Pschorr's method (A., 1902, i, 96), and the dry isomerides (84% yield) were extracted with hot benzene and filtered at 40—50° from the insoluble 6-nitro-3-hydroxybenzaldehyde, m. p. 166°. The mother liquor was then left to crystallise until the brownish nodules which first separated began to be mixed with pale yellow tablets. The latter form the known 4-nitro-3-hydroxybenzaldehyde, m. p. 128°. The impure brownish substance was then distilled in steam, which removed the last-named aldehyde much more readily than the third, new, 2-nitro-3-hydroxybenzaldehyde.

6-Nitro-3-hydroxybenzaldehyde is the most readily soluble in water and least readily soluble in benzene or chloroform of the three. The *acetate*, $CHO\cdot C_6H_3(NO_2)\cdot OAc$, forms pale yellow needles, m. p. 74°, the *benzoate*, yellow needles, m. p. 103°, and the *carbonate*,

$$[CHO\cdot C_6H_3(NO_2)\cdot O]_2CO,$$

prepared by the action of carbonyl chloride on cold dilute solutions in sodium carbonate, separates in small, rhombic crystals, m. p. 202°; these esters are most readily hydrolysed by alkalis. The *p-toluenesulphonate*, $C_{14}H_{11}O_6NS$, forms very stout, pale prisms, m. p. 94°, and the *diphenylcarbamate*, $CHO\cdot C_6H_4(NO_2)\cdot O\cdot CO\cdot NPh_2$, crystallises in glistening leaflets, m. p. 138°.

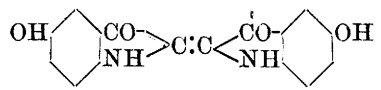
4-Nitro-3-hydroxybenzaldehyde is the least readily soluble in water and most easily soluble in benzene and chloroform of the three isomerides. The constitution has been definitely established by oxidising the *p-toluenesulphonate*, large cubes, m. p. 102°, to the

corresponding *ester* of 4-nitro-3-hydroxybenzoic acid, $C_{14}H_{11}O_7NS$, m. p. 160—161°, by means of a concentrated solution of permanganate in glacial acetic acid.

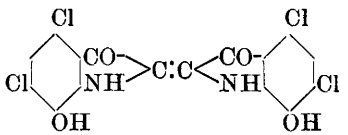
2-*Nitro*-3-*hydroxybenzaldehyde*, $C_7H_5O_4N$, forms almost colourless needles, m. p. 152°, and yields a p-*toluenesulphonate*, rhombic crystals, m. p. 112°. Its constitution is proved by methylation to the known 2-nitro-3-methoxybenzaldehyde.

6-Chloro-3-hydroxybenzaldehyde, prepared by Raschig by chlorinating the carbonate of *p*-chloro-*m*-cresol, according to his patent, D.R.-P. 232071 (A., 1911, i, 537), forms long needles; the *methyl ether* has m. p. 63°, and yields the known 6-chloro-3-methoxybenzoic acid, m. p. 170—171°, on oxidation. It was nitrated (D 1·3) in 50% acetic acid at 50—75°, and the product separated by taking advantage of the facts that the *o*-nitroaldehyde forms a sparingly soluble potassium salt and the *p*-derivative is volatile in steam. 3-*Chloro*-2-*nitro*-3-*hydroxybenzaldehyde* forms small needles, m. p. 138°; *methyl ether*, m. p. 148°; p-*toluenesulphonate*, large tablets from benzene, m. p. 155°. 6-*Chloro*-4-*nitro*-3-*hydroxybenzaldehyde* forms slender, pale yellow needles, m. p. 104°. 4 : 6-*Dichloro*-3-*hydroxybenzaldehyde*, prepared from the carbonate of dichloro-*m*-cresol according to Raschig, D.R.-P. 233631, has m. p. 130°, and gives a *methyl ether*, m. p. 117°. Its nitration product, 4 : 6-*dichloro*-2-*nitro*-3-*hydroxybenzaldehyde* forms stout crystals, m. p. 157°, and yields a *methyl ether*, m. p. 69°, and a p-*toluenesulphonate*, $C_{14}H_9O_6NCl_2S$, cubes, m. p. 172°.

The p-*toluenesulphonate*, coppery leaflets from nitrobenzene, and the *diphenylcarbamate*, small needles, of 5 : 5′-dihydroxyindigotin were obtained in good yield from the above esters of 6-nitro-3-hydroxybenzaldehyde. They dye textile fibres remarkably pure greenish-blue shades from a hyposulphite vat. The esters are hydrolysed, however, if the alkaline, alcoholic vat is kept at 100° for some time, a current of coal-gas displacing the air, and 5 : 5′-*dihydroxyindigotin* (annexed formula) is precipitated on adding acetic acid. It forms dark blue needles from pyridine. The p-*toluenesulphonate* of 7 : 7′-dihydroxyindigotin is obtained from the above ester of 2-nitro-3-hydroxybenzaldehyde. It is unnecessary to prepare this ester in order to obtain 7 : 7′-*dihydroxyindigotin*, however, for the free 2-nitro-3-hydroxybenzaldehyde may be dissolved in warm baryta water and then mixed with acetone, when the dye-formation soon begins. The dye forms stout, short needles, and yields the known 7 : 7′-dimethoxyindigotin on methylation.



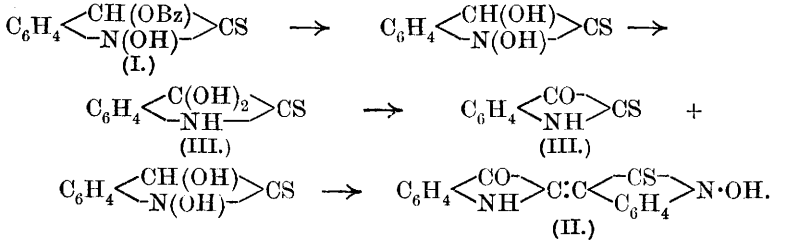
6-Chloro-2-nitro-3-hydroxybenzaldehyde also gives a high yield of 4 : 4′-*dichloro*-7 : 7′-*dihydroxyindigotin* by direct means, steel-blue needles from quinoline, and the p-*toluenesulphonate* is also obtained from the ester of the aldehyde. 4 : 6 : 4′ : 6′-*Tetrachloro*-7 : 7′-*dihydroxyindigotin* (annexed formula) forms compact needles from quinoline; the p-*toluenesulphonate* separates in slender,



brassy crystals, and the methyl ether, *4 : 6 : 4′ : 6′-tetrachloro-7 : 7-dimethoxyindigotin*, forms long, purple needles from nitrobenzene.

J. C. W.

Indigoid Dyes Containing Sulphur. I. Thioindole Derivatives. A Synthesis of Indirubin. AUGUST ALBERT (*Ber.*, 1915, **48**, 474—483).—When the benzoyl derivative of *o*-nitromandelamide is reduced, it is converted directly into benzoyldioxindole (Heller and Mayer, A., 1906, i, 585). It was thought that the benzoyloxy-*o*-nitrophenylthioacetamide (this vol., i, 539) would undergo a similar change. It has been found that when the benzoyl derivative of *o*-nitrobenzaldehydecyanohydrin is treated with ammonium sulphide, instead of thioacetic acid, besides combining with hydrogen sulphide it also suffers reduction of the nitro-group to the hydroxylamino-group. The resulting *α*-benzoyloxy-*o*-hydroxylaminophenylthioacetamide behaves as a weak acid. It is very readily condensed, with the elimination of ammonia, to 2-thio-1-hydroxy-3-benzoyloxy-2 : 3-dihydroindole (I) by shaking with dilute hydrochloric acid. An excess of sodium hydroxide causes the same liberation of ammonia, but the indole compound is then condensed further to a mixture of dyes, with the elimination of benzoic acid. The mixture contains the soluble sodium salt of a thio-compound (II) closely related to indirubin, whilst the insoluble part contains indigotin. The presence of two hydroxyl groups might have been expected, and the reaction must therefore be expressed by the changes:



The formation of indigotin is the result of the condensation of two molecules of the thioisatin (III), but this side-reaction is minimised by keeping the temperature low.

α-Benzoyloxy-*o*-nitrophenylacetonitrile was dissolved in benzene, mixed with a concentrated alcoholic solution of ammonia, and then saturated with dry hydrogen sulphide at 0°. After leaving the well-stoppered vessel in the cold overnight, the product was filtered and crystallised from alcohol. *α-Benzoyloxy-o-hydroxylaminophenylthioacetamide*, $OH\cdot NH\cdot C_6H_4\cdot CH(OBz)\cdot CS\cdot NH_2$, separates in slender, long, sharp tablets, with $1EtOH$ and $0{\cdot}5H_2O$, m. p. 159—164° (according to the rate of heating). It forms a sparingly soluble sodium salt when dissolved in warm *N*-sodium hydroxide (1 mol.). *2-Thio-1-hydroxy-3-benzoyloxy-2 : 3-dihydroindole* (I) crystallises with 1MeOH in colourless needles, m. p. of alcohol-free substance, 97—98°, and forms an *acetyl* compound, $C_{17}H_{13}O_4NS$, m. p. 106—108°. It was covered with about 0·5*N*-sodium hydroxide (90 c.c. to 5 grams) and left in the cold,

when a mass of ciliated, blue needles separated. The greater part of this dissolved in water, leaving indigotin and, probably, indirubin. The solution was treated with carbon dioxide and the dye crystallised from carbon disulphide. 2-*Indoxyl*-3 : 1-*hydroxythioindole* (II) is bluish-violet, dyes wool greyish-violet from hyposulphite vats, explodes above 160°, and forms a *benzoyl* compound, long, very dark blue needles, decomp. 155—161°.

Indirubin itself can be obtained by warming 2-thio-1-hydroxy-3-benzoyloxy-2 : 3-dihydroindole with sodium hydrogen carbonate and sodium sulphide. J. C. W.

A New Synthesis of Phenazine. ALFRED ECKERT and KARL STEINER (*Monatsh.*, 1914, **35**, 1153—1155).—In a previous paper (this vol., i, 567) the authors have shown that the reduction of nitrodianthraquinonylamines in acid solution gives rise to indanthren derivatives. A similar internal condensation, resulting in the formation of phenazine, is now shown to occur during the reduction of 2 : 2′-dinitrodiphenylamine. The latter compound is readily prepared by heating a mixture of *o*-nitroaniline, *o*-bromoaniline, and sodium carbonate in nitrobenzene solution in the presence of a trace of cuprous chloride. Its conversion into phenazine is effected by reduction with stannous chloride and hydrochloric acid in acetic acid solution, and subsequent oxidation of the resulting quinhydrone by hydrogen peroxide, potassium permanganate or ferric chloride. F. B.

The Decoloration of Magenta Solutions by Amorphous Carbon. A. B. DROOGLEEVER FORTUYN (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1322—1325).—It has been found that an aqueous solution containing 0·01% of new-magenta, from which the colour has been almost completely discharged by the action of charcoal, shows a return of the red colour when the filtered solution has been kept for some time. The phenomenon cannot be attributed to impurities in the charcoal, for the effect was observed with charcoal which had been boiled with 25% hydrochloric acid and subsequently treated with ammonia and washed thoroughly with distilled water. The addition of a little acetic acid accelerates the return of the colour. A similar effect has been observed with solutions of acid magenta. The phenomenon depends to some extent on the nature of the carbon, and was not observed with certain impure varieties of animal charcoal.

H. M. D.

Reaction of Aldehydes with *s*-Diphenylcarbazide. New Method of Preparing Substituted Hydroxytriazoles. BERNARDO ODDO and E. FERRARI (*Gazzetta*, 1915, **45**, i, 238—262).—In acetic acid solution containing fused sodium acetate, aldehydes condense readily with *s*-diphenylcarbazide, forming derivatives of 1-phenyl-1 : 2 : 4-triazole-3-one or of the tautomeric 3-hydroxy-1-phenyl-1 : 2 : 4-triazole, together with aniline :

(1) $NHPh\cdot NH\cdot CO\cdot NH\cdot NHPh + R\cdot CHO = H_2O + NHPh<\begin{matrix}CHR\cdot NPh\\ CO—NH\end{matrix}$,

and (2) the latter $=NH_2Ph + N\leqslant^{CR\cdot NPh}_{CO\cdot NH} \longrightarrow NPh\langle^{CR:N}_{N=C\cdot OH}$.

Since, with ketones, this reaction would yield, not aniline, but a derivative of it, NHPhR, it serves as a sensitive means of detecting compounds exhibiting aldehydic functions. When boiled with glacial acetic acid and fused sodium acetate, *s*-diphenylcarbazide alone yields only minimal traces of aniline.

The velocity of the reaction varies markedly with different aldehydes. Thus, with salicylaldehyde, the yield of triazole does not approach that obtained with other aldehydes, namely, 70—90%, even after prolonged heating. A nitro-group in the ortho-position exerts a retarding action. The reaction succeeds with furfuraldehyde, aniline being separable. With dextrose, difficulty is encountered in the purification of the glucosohydroxyphenyltriazole, but a nitrogenous compound is obtained in the form of a brick-red powder, m. p. about 180° (decomp.). With dialdehydes, such as glyoxal, double hydroxytriazole nuclei, such as $OH\cdot C(N\cdot NPh)\!-\!N\geqslant C\cdot C\leqslant N\!-\!C(NPh\cdot N)\cdot OH$, appear to be formed. Arabinose gives the compound $CH(CH\cdot CH\!-\!O)\geqslant C\cdot C\leqslant N\!-\!C(NPh\cdot N)\cdot OH$, which is identical with that yielded by furfuraldehyde.

Benzaldehyde and *s*-diphenylcarbazide yield 3-hydroxy-1 : 5-diphenyl-1 : 2 : 4-triazole or 1 : 5-diphenyl-1 : 2 : 4-triazole-3-one, which was obtained by Young and Annable by the oxidation of a mixture of benzaldehyde and phenylsemicarbazide with ferric chloride (T., 1897, **71**, 200). This compound does not react with phenylhydrazine, but gives the enolic reaction with ferric chloride and forms an acetyl derivative, m. p. 133°. As is the case with the triazole derivatives described below, the hydrochloride is not formed in quantitative yield and, on exposure to air, gradually loses all its hydrogen chloride; with the alkaloid reagents, the hydrochloride gives precipitates of various colours. The action of dry hydrogen chloride on a suspension of the base in anhydrous ether yields the *dihydrochloride*, $C_{14}H_{13}ON_3,2HCl$, which is obtained as a white, crystalline powder with a yellow reflection and begins to blacken at about 200° and melts at the same temperature as the base itself, 288°.

3-*Hydroxy*-1-*phenyl*-5-p-*tolyl*-1 : 2 : 4-*triazole*, $OH\cdot C(N\cdot NPh)\!-\!N\geqslant C\cdot C_6H_4Me$,

obtained from *s*-diphenylcarbazide and *p*-tolualdehyde, forms white needles, m. p. 275—276°. Its *acetyl* derivative, $C_{17}H_{15}O_2N_3$, forms minute, white needles, m. p. 107°; the *hydrochloride*, $C_{15}H_{13}ON_3,HCl,2H_2O$, white crystals, melting without apparent charge at 275°, and the *aurichloride*, $C_{15}H_{13}ON_3,HAuCl_4,H_2O$, a yellow, crystalline precipitate, contracting at 83°, becoming pasty at 102°, and melting sharply at 133°. The hydrochloride gives yellowish-white, curdy-white and brick-red precipitates with cadmium and potassium iodides, mercuric and potassium iodides, and bismuth and potassium iodides respectively.

3-*Hydroxy*-1-*phenyl*-5-o-*hydroxyphenyl*-1 : 2 : 4-*triazole*, $C_{14}H_{11}O_2N_3$, obtained from salicylaldehyde, forms white needles, m. p. 297° (decomp.), and its *diacetyl* derivative, $C_{14}H_9O_2N_3Ac_2$, small needles, has m. p. 100°.

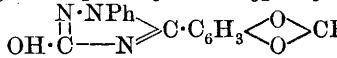
3-*Hydroxy*-1-*phenyl*-5-o-*methoxyphenyl*-1 : 2 : 4-*triazole*, $C_{15}H_{13}O_2N_3$, obtained from *o*-anisaldehyde, forms minute, white needles, m. p. 300°; its *acetyl* derivative, $C_{15}H_{12}O_2N_3Ac$, which forms white, prismatic needles, m. p. 112°, and its *hydrochloride* (+HCl) were prepared.

3-*Hydroxy*-1-*phenyl*-5-o-*nitrophenyl*-1 : 2 : 4-*triazole*, $C_{14}H_{10}O_3N_4$, obtained from *o*-nitrobenzaldehyde, forms yellow prisms, m. p. 243—244°, and yields a dense, oily acetyl derivative.

3-Hydroxy-1-phenyl-5-*m*-nitrophenyl-1 : 2 : 4-triazole, obtained from *m*-nitrobenzaldehyde, agrees in properties with the compound obtained by oxidising a mixture of *m*-nitrobenzaldehyde and phenylsemicarbazide with ferric chloride (compare Young and Annable, *loc. cit.*).

3-Hydroxy-1-phenyl-5-β-phenylethenyl-1 : 2 : 4-triazole, obtained from cinnamaldehyde, has been already prepared by Widman (A., 1896, i, 629); its *acetyl* derivative has been prepared.

3-*Hydroxy*-1-*phenyl*-5-m : p-*methylenedioxyphenyl*-1 : 2 : 4-*triazole*,



obtained from piperonaldehyde, forms minute, white needles, m. p. 274°; its *acetyl* derivative, $C_{15}H_{10}O_3N_3Ac$, m. p. 123°, *mono*- and *di*-*hydrochlorides* were prepared.

3-*Hydroxy*-1-*phenyl*-5-p-*hydroxy*-m-*methoxyphenyl*-1 : 2 : 4-*triazole*, $C_{15}H_{13}O_3N_3$, prepared from vanillin, forms soft, minute, prismatic needles, m. p. 299—301°; its *diacetyl* derivative, which forms tufts of white needles, m. p. 149°, and its *hydrochloride*, $C_{15}H_{13}O_3N_3,HCl,2H_2O$, were prepared. T. H. P.

The Diketotriazines. Synthesis of Substituted Semicarbazides. J. Bougault (*Compt. rend.*, 1915, **160**, 625—627).—The mono-esters of diketotriazines (compare A., 1914, i, 1004, 1205) when acted on by dilute sodium hydroxide, and the product treated with concentrated hydrochloric acid in the cold, yield substituted semicarbazides of the type $NH_2{\cdot}NH{\cdot}CO{\cdot}NHR$. It is preferable to replace the sodium hydroxide by sodium carbonate to avoid decomposition of the intermediate product. In this way 4-methyl-2-benzyldiketotriazine treated with the alkali yielded the *methylsemicarbazone* of phenylpyruvic acid, m. p. 194°, which with hydrochloric acid gave *methylsemicarbazide*, $NH_2{\cdot}NH{\cdot}CO{\cdot}NHMe$, m. p. 112°. 4-Ethyl-2-benzyldiketotriazine gave in turn the *ethylsemicarbazone* of phenylpyruvic acid, m. p. 141°, and *ethylsemicarbazide*, m. p. above 100°. 2 : 4-Dibenzyldiketotriazine gave with alkali a mixture of the *α-benzylsemicarbazone*, m. p. 168°, and *β-benzylsemicarbazone*, m. p. 170°, of phenylpyruvic acid separable through their *sodium* salts, that of the former being soluble in water, and that of the latter very sparingly soluble. Both of these semicarbazones with hydrochloric acid yielded the same *benzylsemicarbazide*, m. p. 111°. All these substituted semicarbazides are stable, crystalline substances soluble

in water, alcohol and chloroform, and give crystalline hydrochlorides soluble in water and alcohol. They appear to behave towards aldehydes and ketones in the same way as semicarbazide itself.

W. G.

Constitution of the Internal Diazo-oxides (Diazophenols). GILBERT T. MORGAN and JAMES WALKER PORTER (T., 1915, **107**, 645—659).—The constitution of the internal diazo-oxides (the so-called diazophenols) has been represented by the *eso*-diazo-oxide formula $R<^{O}_{N}>N$, the quinonediazide formula $R<\!\!<^{O}_{N_2}$, and recently (Klemenc, A., 1914, i, 743) by the diazonium formula $R<^{O}_{N:N}$. These three formulæ are discussed and evidence is adduced which indicates that the last is inadmissible, and that the quinonediazide formulation, although not entirely excluded, is less generally serviceable than the *eso*-diazo-oxide structure.

2-*Nitrobenzene*-4-*diazo*-1-*oxide*, $NO_2 \cdot C_6H_3<^{O}_{N}>N$, crystallises in yellow leaflets and decomposes violently at 168°. It may be prepared either by the diazotisation of 2-nitro-4-aminophenol or by the following method. On diazotising 4-chloro-3-nitroaniline in moderately concentrated hydrochloric or sulphuric acid, 4-chloro-3-nitrobenzenediazonium chloride or sulphate is produced, and may be obtained in colourless crystals by adding alcohol and ether to the acid solution; if, however, the acidity of the solution is diminished by dilution, partial neutralisation, or the addition of sodium acetate, the liquid becomes yellow and 2-nitrobenzene-4-diazo-1-oxide separates. The diazo-oxide couples readily with alkaline β-naphthol to form 3-*nitro*-4-*hydroxybenzeneazo*-β-*naphthol*, $NO_2 \cdot C_6H_3(OH) \cdot N:N \cdot C_{10}H_6 \cdot OH$, m. p. 216°, which crystallises in orange-red leaflets; its alkali salts give deep crimson solutions in water. It also couples with alkaline resorcinol, forming an orange azo-derivative which gives a deep red solution with alkali hydroxide, and with tolylene-2 : 4-diamine with production of a brown azo-compound which yields a deep orange-red solution in potassium hydroxide. The diazo-oxide does not couple readily with β-naphthylamine, but if it is added to a solution of this base in dilute acetic acid, an *azo*-derivative, m. p. 226°, is produced, which forms bright red needles.

3-*Nitrobenzene*-4-*diazo*-1-*oxide* is not precipitated when sodium acetate or sodium hydrogen carbonate is added to the product obtained by the diazotisation of 3-nitro-4-aminophenol in hydrochloric acid solution, but is best prepared by treating this aminophenol with nitrous fumes in ethereal solution. The diazo-oxide forms brown crystals and explodes with moderate violence at 119°. It couples with resorcinol in presence of a trace of alkali with production of 2-*nitro*-4-*hydroxybenzeneazoresorcinol*, $NO_2 \cdot C_6H_3(OH) \cdot N:N \cdot C_6H_3(OH)_2$, m. p. 212° (decomp.), which forms brownish-red crystals.

5-*Nitrobenzene*-2-*diazo*-1-*oxide*, prepared from 5-nitro-2-aminophenol, crystallises in garnet-red prisms; it darkens at 95°, becomes black at 105°, and decomposes extremely violently at 111°. It couples with

β-naphthol to form 4-*nitro*-2-*hydroxybenzeneazo*-β-*naphthol*, a bright red compound which yields intensely coloured metallic *salts*.

Certain *m*-aminophenols were treated according to the methods by which *o*- and *p*-diazo-oxides had been obtained from the *o*- and *p*-aminophenols. 4-Nitro-, 6-nitro-, and 4 : 6-dinitro-3-aminophenols were diazotised in various ways, but no indication of the formation of *m*-diazo-oxides was obtained. The diazonium salts gradually decomposed into tarry, uncrystallisable products; they were characterised by conversion into azo-derivatives. 4-*Nitro*-3-*hydroxybenzeneazoresorcinol*,

$$NO_2 \cdot C_6H_3(OH) \cdot N{:}N \cdot C_6H_3(OH)_2,$$

m. p. 196°, forms dark red crystals. 2-*Nitro*-5-*hydroxybenzeneazo*-β-*naphthol*, $NO_2 \cdot C_6H_3(OH) \cdot N{:}N \cdot C_{10}H_6 \cdot OH$, is a red compound which does not melt below 260°. 2 : 4-*Dinitro*-5-*hydroxybenzeneazo*-β-*naphthol*, $OH \cdot C_6H_2(NO_2)_2 \cdot N{:}N \cdot C_{10}H_6 \cdot OH$, forms brownish-red needles, and does not melt below 260°. E. G.

Coagulation of Albumin by Electrolytes. WILDER D. BANCROFT (*J. Physical Chem.*, 1915, **19**, 349—359).—A theoretical paper in which the statement of Pauli and Hirschfeld (A., 1914, i, 753) that albumin forms definite compounds with acids and bases is discussed. It is shown that the data, so far as they go, can be more satisfactorily accounted for on the assumption that adsorption is being dealt with, than on the assumption that albumin is an amphoteric electrolyte. Slightly acid or alkaline solutions of albumin are least stable when they are electro-neutral as regards the disperse phase. Since the sign of the electrical charge depends on the preferential adsorption of cation or anion, the nature of both ions becomes important. When albumin is positively charged, the most strongly adsorbed anion will be effective in causing precipitation, and the most strongly adsorbed cation in preventing precipitation. The reverse will be the case when albumin is negatively charged. If a salt consisting of a readily adsorbed cation and a slightly adsorbed anion is added to a negatively charged albumin sol, precipitation will occur at low concentrations, but not at high concentrations, but in the latter case the albumin will have become positively charged. The reversibility of precipitation depends in part on the ease with which the precipitating agent can be washed out, but it seems probable that in the case of albumin the physical properties of the precipitate are important as determining coalescence and agglomeration. In the case of albumin free from electrolyte it must be assumed that the stability of the solution is due to the peptonising action of water in the absence of electrolytes. The coagulation of albumin is to be regarded as a typical and general case, whereas the coagulation of gold and ferric oxide sols are special cases.

J. F. S.

A Method for the Decomposition of the Proteins of the Thyroid, with a Description of Certain Constituents. E. C. KENDALL (*J. Biol. Chem.*, 1915, **20**, 501—509).—These proteins may be hydrolysed by 1% sodium hydroxide in 90% alcohol; of the products, some (*A*) are precipitable by acids, whilst others (*B*) are soluble in acids. Iodine is evenly divided between the two, but those in *A* are

essentially acidic. After the removal of tryptophan, tyrosine, and lauric acid, the percentage of iodine rises, and from the remainder a crystalline compound was isolated containing 60% of iodine. *B* consists of amino-acid complexes, mostly precipitable by 40% ammonium sulphate, and easily dialysable; there is also a compound which reduces silver and mercury salts. The physiological activity of the thyroid is still retained in both *A* and *B*. *B* produces no toxic symptoms, and the reducing substance in it relieves muscle cramp. *A* produces toxic effects, and the severity of the symptoms (nausea, diarrhœa, headache, increased pulse rate, etc.) depends on the iodine content.

W. D. H.

Colloidal Swelling of Wheat Gluten. Fred W. Upson and J. W. Calvin (*J. Amer. Chem. Soc.*, 1915, **37**, 1295—1304).—Wood and Hardy (A., 1909, i, 341) have shown that wheat gluten is an emulsoid colloid and that when in contact with a solution its properties depend on the concentration of acid and salts in the solution. A study has now been made of the changes which take place in the hydration capacity of the colloid.

It has been found that moist gluten absorbs water from acid solutions in quantity varying with the nature and concentration of the acid. The presence of neutral salts retards the absorption of water and in high concentrations may even cause a loss of water from moist gluten. If gluten which has absorbed water in an acid solution is transferred to a salt solution, it loses water and regains its original physical properties. Non-electrolytes are much less effective than electrolytes in inhibiting the swelling of gluten in acid solutions. E. G.

The Oxidation of Keratin Sulphur and Cystine Sulphur by Potassium Permanganate. Th. Lissizin (*Biochem. Bull.*, 1915, **4**, 18—23).—A much larger amount of sulphur is split off from cystine as sulphuric acid than from keratin (prepared from hair); in the oxidation of keratin, the bulk of the sulphur remains in an organic combination soluble in water; only 10% is converted into sulphuric acid; 47% of the sulphur in cystine is changed into sulphuric acid.

W. D. H.

Chondroitin-sulphuric Acid. IV. P. A. Levene and F. B. La Forge (*J. Biol. Chem.*, 1915, **20**, 433—444. Compare A., 1914, i, 889).—Chondrosamine on oxidation with bromine gives *chondrosamic acid*, $C_6H_{13}O_6N$, short, prismatic needles, joined together in rosettes, from 50% alcohol. It does not melt, but darkens slowly above 190°, $[\alpha]_D^{28\cdot5}$ – 16·15°, and after forty-eight hours $[\alpha]_D^{25}$ – 29·23°. Chondrosamic acid is different from glucosamic acid, but on reduction with hydriodic acid both acids give the same aminohydroxyhexoic acid (Fischer and Tiemann, A., 1894, i, 168), which proves that chondrosamine also contains a normal carbon chain.

Chondrosic acid, $C_6H_8O_7$, has been prepared from the calcium salt already described (*loc. cit.*) by treatment with oxalic acid. It crystallises in large parallelopipeds, m. p. 179—181° (decomp.), soluble in water and alcohol, nearly insoluble in ether, $[\alpha]_D^{28}$ – 16·56°. Chondrosic acid

on heating in a sealed tube with hydrochloric and hydrobromic acids forms furan-2 : 5-dicarboxylic acid, whilst heating alone in an atmosphere of carbon dioxide gives furan-2-carboxylic acid. It, therefore, closely resembles *iso*saccharic acid, which when similarly treated gives the same compounds. An isomeric but inactive dicarboxylic acid is obtained from chondrosamine by converting it into chondrosamic acid and then treating with nitrous acid. epi-*Chondrosic acid*, $C_6H_8O_7$, has m. p. 201—202°. From these and the results previously obtained, the conclusion is reached that chondrosamine has the structure of *l*-α-allosamine.

An attempt to synthesise glucosamic acid by the addition of hydrogen cyanide to ribosimine, with subsequent hydrolysis, was unsuccessful. The product is a *new hexosamic acid*, $C_6H_{13}O_6N$, short, prismatic needles from 50% methyl alcohol, m. p. 198°, $[\alpha]_D^{28}$ at once $-22{\cdot}26°$, after forty-eight hours $-9{\cdot}4°$.

When glucosamic acid is treated first with nitrous acid and then with nitric acid an isomeric *iso*saccharic acid, epi-*isosaccharic acid*,

$$C_6H_8O_7 + H_2O,$$

is formed in large, crystalline plates. The substance becomes anhydrous when heated in a vacuum at 78° and then melts at 160°, $[\alpha]_D^{28} + 39{\cdot}70°$. The *potassium* salt contains $\frac{1}{2}H_2O$, and the *lead* salt, $2H_2O$.

H. W. B.

The Separation and Determination of Peptones by their Solubility in Methyl and Ethyl Alcohols. E. VLĂHUȚĂ (*Bull. Acad Română*, 1914/5, **3**, 290—300).—The author has prepared the peptones resulting from the partial hydrolysis of a number of different proteins obtained from various sources, using Fischer's method, and has separated the peptones into four fractions, varying in their solubilities in methyl alcohol. The protein material was added in small quantities to 70% sulphuric acid at 0° with constant stirring, and kept at this temperature for two hours. The mixture was kept for three days at the ordinary temperature with frequent stirring and then poured into twenty litres of distilled water at 0°, and the sulphuric acid was just completely precipitated with barium hydroxide. The barium sulphate was filtered off and the filtrate evaporated to dryness at 35—40° under reduced pressure (15 mm.). The peptone residue was divided into four fractions as follows: the peptone was extracted with hot methyl alcohol and filtered, the insoluble portion being fraction I. The filtrate on standing twenty-four hours gave a deposit, fraction II, which was filtered off. The filtrate on dilution with an equal volume of ethyl alcohol gave a further deposit, fraction III, and the filtrate from this on evaporation in a vacuum at 35—40° left a residue, fraction IV. These four fractions, of which all but the first were invariably easily soluble in water, were tested in aqueous solution by the biuret reaction, Millon's reagent, for cystine, for tryptophan and for precipitation with the usual protein precipitants. In addition the ash content was determined and the optical rotation measured. This method was applied to the gluten of wheat, the protein of beef, the protein of fish, the albumin of eggs, the casein of milk and keratin, the results being

set out in detail. The results obtained show that the peptones bear the mark of their origin. Thus, from proteins rich in cystine or tyrosine, peptones were obtained also rich in these substances and vice versa. W. G.

The Influence of Low Temperatures on Enzymes. Joseph Samuel Hepburn (*Biochem. Bull.*, 1915, **4**, 136—150).—A useful review of previous work on the subject. W. D. H.

Physiological Activity of Combined Hydrochloric Acid. J. H. Long (*J. Amer. Chem. Soc.*, 1915, **37**, 1333—1347).—Although a large amount of work has been done on the efficiency of combined hydrochloric acid in the digestion of proteins by pepsin, certain points have not been fully studied. Experiments have now been made to compare the digestive activity of hydrochloric acid when combined with betaine or glutamic acid with its activity when combined with complex proteins.

The hydrochlorides of betaine and glutamic acid are sufficiently dissociated in aqueous solution to enable the acid to aid pepsin in the rapid digestion of egg-albumin or fibrin. In the case of the betaine salt the action is almost equal to that of dilute hydrochloric acid of a concentration corresponding with the total hydrogen chloride concentration of the betaine hydrochloride solution. With glutamic acid the action is somewhat slower. In both cases, in the mixture of coagulated protein and the hydrochloride, a part of the hydrogen chloride leaves the latter and becomes attached to the protein.

Mixtures containing protein combined with hydrochloric acid are much less active and hold scarcely enough acid to digest themselves perfectly. If further quantities of protein are added, with pepsin, digestion becomes very slow. When the protein and hydrochloric acid are so related as to bring the hydrogen ion concentration down to $P_H = 2{\cdot}96$, the rate of digestion is slow. The maximum activity is reached when $P_H = 1{\cdot}69$, digestion at this point being very rapid. Between these limits all degrees of digestive activity occur. Dry preparations of protein and hydrochloric acid about midway between these limits cease to be physiologically active. E. G.

Action of Erepsin. Frank E. Rice (*J. Amer. Chem. Soc.*, 1915, **37**, 1319—1333).—As the properties of erepsin and its action as an enzyme have not been studied hitherto to the same extent as its physiological significance, the present work was undertaken.

Witte's peptone is readily hydrolysed by erepsin, the quantity of amino-nitrogen split off varying with the amount of peptone in solution. The extent of the hydrolysis by moderate quantities of erepsin during the first ten hours is directly proportional to the time, and the quantity of amino-nitrogen split off during this period is proportional to the weight of erepsin raised to the three-fourths power. Erepsin is completely adsorbed from acid, alkaline, and neutral solutions by aluminium hydroxide, and is also adsorbed by kaolin from acid solutions, but not from neutral or alkaline solutions. The enzyme attacks fibrin in very weakly alkaline solutions, but the action is

inhibited by sodium hydroxide in a concentration of 1·5 c.c. of 0·2*N*-solution per 50 c.c. Gelatin is rapidly hydrolysed by erepsin. It has been found that erepsin attacks the tissue of the mucous lining of the small intestine and is probably the enzyme, or one of the enzymes, inducing autolysis of that tissue. Erepsin is best preserved in neutral, aqueous solution. E. G.

Amylases. X. Comparison of Certain Properties of Pancreatic and Malt Amylase Preparations. H. C. SHERMAN and M. D. SCHLESINGER (*J. Amer. Chem. Soc.*, 1915, **37**, 1305—1319).—The work described in this paper was undertaken with the object of ascertaining whether the amylases obtained from the pancreas and from malt should be regarded as identical or as distinct substances. The results show that they are similar in physical properties, show the same qualitative reactions, and contain the same percentage of nitrogen, distributed in the same way among the different types of amino-acid radicles. Nevertheless, they exhibit the following differences which indicate that they are not identical.

Malt amylase is most active in an acid solution, whilst pancreatic amylase shows the greatest activity in an alkaline solution. When allowed to act on soluble starch under the optimum conditions of reaction and salt concentration, pancreatic amylase is much more active than malt amylase. Pancreatic amylase exerts a marked proteolytic action on casein and gelatin, whereas malt amylase does not exhibit any proteolytic activity. In purified pancreatic amylase, the amyloclastic and saccharogenic powers are concentrated in almost the same ratio, but purified malt amylase of high saccharogenic activity does not show a correspondingly high amyloclastic power. In the case of each amylase, the rate at which the activity deteriorates increases with the temperature and also with the dilution, but when aqueous solutions of the amylases are left at the ordinary temperature, the malt amylase is always more stable than that of the pancreas. Pancreatic amylase, however, is more stable than malt amylase in 50% alcohol and shows a more sustained activity in long digestion experiments in which a relatively large amount of substrate is present together with such a concentration of activating electrolytes as is found best adapted to each enzyme in the ordinary determination of diastatic power. The amylases deteriorate during dialysis, and much more rapidly at the ordinary temperature than at 5—10°. The increase in the deterioration over that which takes place when the enzymes are merely left in water at the same concentration is more easily demonstrable in the case of malt amylase.

The chemical nature of these enzymes is discussed. E. G.

Comparative Study of the Influence of Acetic Acid on the Synthesising and Hydrolysing Properties of α-Glucosidase (Glucosidase of Bottom Yeast, Dried in the Air). EM. BOURQUELOT and A. AUBRY (*Compt. rend.*, 1915, **160**, 742—745; and *J. Pharm. chim.*, 1915, [vii], **12**, 15—22).—The authors have examined the effect of adding small quantities of acetic acid (0·0 to 0·1%) to the aqueous medium on the synthesising and hydrolysing actions of α-glucosidase. With identical experimental

conditions, the media containing the same proportion of methyl alcohol, the injurious influence of acetic acid is the same for each of the two opposed properties of α-glucosidase. Up to 0·01% the acid has no influence, but with 0·02% both reactions are stopped before the normal equilibrium is reached. In media containing above 0·04% acetic acid, neither of the actions takes place, this being due to the destruction of the enzyme by the acid. W. G.

Alfalfa [Lucerne] Laccase. HERBERT B. BUNZEL (*J. Biol. Chem.*, 1915, **20**, 697—706).—The effect of salts of strong bases with weak acids on the rate of oxidation of quinol by atmospheric oxygen is due entirely to the concentrations of hydroxyl ions in such solutions. There is no quinol-oxidising oxydase or laccase in *Medicago sativa*. The accelerating effect of Euler and Bolin's laccase prepared from *M. sativa* on the rate of oxidation of quinol by atmospheric oxygen is due to the alkalinity of the solutions of the salts contained in their preparations. W. D. H.

Oxydases. VII. Action of Carbonic Acid on Tyrosinase. R. CHODAT and K. SCHWEIZER (*Arch. Sci. phys. nat.*, 1915, [iv], **39**, 327—331. Compare A., 1912, ii, 399, 611; 1913, i, 411).—It has been previously shown (A., 1913, i, 411) that tyrosinase acts on an amino-acid to form ammonia, carbon dioxide, and an aldehyde containing one carbon atom less than the original acid. Tyrosinase is very sensitive to the influence of acids, and it is now shown that its activity is depressed by exposure to carbonic acid even in presence of glycine. On the other hand, the action is not retarded if tyrosinase and glycine are added to a solution of *p*-cresol saturated with carbon dioxide. The ferment is not altered, as the adsorption complex may be destroyed by shaking until the original activity is restored. Previous treatment of an extract of tyrosinase with hydrogen for some hours enables it to withstand the action of carbon dioxide for an hour without loss of activity.

Proof of some combination between the oxidising engyme and substrate is afforded by the following experiment: a mixture of tyrosinase, *p*-cresol, and glycine was kept saturated with hydrogen for one hour to prevent oxidation; on allowing access of air, a red coloration was produced in five minutes, whereas in a control experiment in which access of air was allowed immediately after mixing, thirty minutes were required for the same amount of action. E. F. A.

Oxydases. VIII. The Production of Benzaldehyde by Tyrosinase. R. CHODAT and K. SCHWEIZER (*Arch. Sci. phys. nat.*, 1915, [iv], **39**, 331—334).—The formation of formaldehyde by the action of tyrosinase on glycine is very largely accelerated by the presence of chloroform. The same applies to the production of benzaldehyde from phenylglycine and serves to explain the formation of aromatic aldehydes from protein degradation products in plants.

E. F. A.

Oxydases. IX. Use of Peroxydase as a Reagent in Studying Photolysis by means of Chlorophyll. R. CHODAT and K. SCHWEIZER (*Arch. Sci. phys. nat.*, 1915, [iv], **39**, 334—338).—It is claimed that chlorophyll in presence of carbon dioxide in the light gives rise to formaldehyde and to a corresponding amount of hydrogen peroxide, the formation of which may be followed experimentally by means of peroxydase and some oxidisable substance such as pyrogallol or *p*-cresol. Green parts of leaves of *Aspidistra* contain more catalase than the white parts. Etiolated leaves grown in the dark contain less catalase than when grown in the light. E. F. A.

Arginase: Action of Arginase on Creatine. III. ANTONINO CLEMENTI (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 483—489).—In agreement with the observation of Dakin (A., 1907, i, 1099), the author finds that arginase is incapable of resolving creatine into carbamide and sarcosine, so that this enzyme is not able to detach the guanidine residue from every molecule containing it. A false impression would, therefore, result from the replacement of the term arginase by deguanidase, as suggested by Abderhalden ("Lehrbuch der physiologischen Chemie," Berlin, 1914). From the inability of arginase to hydrolyse creatine, it would appear that the action of this enzyme is specific in character. T. H. P.

A Dry Urease Preparation and some Properties of Soja Urease. MARTIN JACOBY and SUGGA (*Biochem. Zeitsch.*, 1915, **69**, 116—126).—The permanent preparation was made from ground soja beans, which were extracted with light petroleum and then with water; the aqueous extract was then evaporated to dryness in a stream of air at 30—40°. This preparation on treatment with alcohol soon becomes insoluble in water without losing its activity. The solution in water when heated at 60° for half an hour becomes only slightly less active; at 70°, however, the ferment is rapidly injured. The ferment is not appreciably injured by treatment with trypsin or papayotin. If the soja-papayotin mixture is dialysed, however, there is a marked diminution of the urease activity; a soja preparation, without papayotin, is not injured by dialysis. Dialysis in the former case appears to remove some auxo-substance. S. B. S.

Resorcinolarsinic Acid and Some of its Derivatives and Products of Reduction. HUGO BAUER (*Ber.*, 1915, **48**, 509—524).—Arsenic acid reacts very readily with resorcinol to form 2 : 4-dihydroxyphenylarsinic acid, the constitution of which is demonstrated by a study of its derivatives. Under the same conditions, catechol, quinol, pyrogallol, and guaiacol are merely oxidised, but the ethers of resorcinol and also the carbethoxy-compound of *m*-aminophenol (future communication), that is, meta-di-derivatives, undergo "arsination." The isolation of the biologically active reduction products was the main interest of the author. This was not possible, however, for the *o*-hydroxyl group confers instability on the arsinic acid, like the *o*-amino-group (Karrer, A., 1914, i, 1100). Certain amino-derivatives were found to be much more stable, and their reduction products are

described. The compounds are very toxic, but have no therapeutic value.

Resorcinol was heated on the water-bath with commercial arsenic acid for two days, when the crystalline mass which separated was crushed with glacial acetic acid and allowed to crystallise slowly from dilute acetic acid. *Resorcinolarsinic acid* [2 : 4-*dihydroxyphenylarsinic acid*], $H_2O_3As{\cdot}C_6H_3(OH)_2$, forms stout, triclinic crystals, m. p. 191°; $a : b : c = 0{\cdot}8088 : 1 : 0{\cdot}4349$, α 84°21·25′, β 104°40·5′, γ 79°31·5′ (Groth and Steinmetz). When nitrated below 0°, it yielded 5-*nitro*-2 : 4-*dihydroxyphenylarsinic acid*, $C_6H_6O_7NAs,2H_2O$, in pale yellow needles, which lost water at 110° and then had m. p. 223° (decomp.), whilst at 60° it formed 3 : 5-*dinitro*-2 : 4-*dihydroxyphenylarsinic acid*,

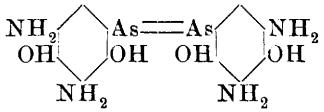
$$C_6H_5O_9N_2As,$$

m. p. 206° (decomp.). Both compounds lost the arsinic acid residue on bromination. the former yielding the known 2 : 6-dibromo-4-nitroresorcinol (Dahmer, A., 1904, i, 871), and the latter, the unknown 6-*bromo*-2 : 4-*dinitroresorcinol*, $C_6H_3O_6N_2Br$, yellow prisms, m. p. 89—90° (2-bromo-4 : 6-dinitroresorcinol is known), which proved the constitution of the arsinic acid and its two nitro-compounds.

The above mononitro-compound was reduced by alkaline hyposulphite to 5-*amino*-2 : 4-*dihydroxyphenylarsinic acid*, $C_6H_8O_5NAs,H_2O$, sheaves of needles, decomp. above 150°; *acetyl* derivative, moderately soluble in water. This compound reduces ammoniacal silver solutions, quickly forms an indophenol dye when the alkaline solution is exposed to the air, and gives a bluish-red azo-dye with resorcinol. The nitro-compound was also reduced by alcoholic stannous chloride, and, after adding glacial acetic acid, the filtrate of the amine salt from a little of the arsenobenzene was dropped into a mixture of hydrochloric acid, glacial acetic acid, and a trace of hydriodic acid, when the *hydrochloride* of 5 : 5′-*diamino*-2 : 4 : 2′ : 4′-*tetrahydroxyarsenobenzene*,

$$NH_2{\cdot}C_6H_2(OH)_2{\cdot}As{:}As{\cdot}C_6H_2(OH)_2{\cdot}NH_2,$$

separated as a dark yellow substance, freely soluble in water. Sodium hydroxide precipitated the free base, which dissolved in excess, and the solution quickly became blue. The *diacetyl* compound was obtained by dissolving the above acetylamino-compound in hypophosphorous acid and shaking with a trace of hydriodic acid, as a yellow powder, insoluble in water. The dinitro-compound was also reduced to 3 : 5 : 3′ : 5′-*tetra-amino*-2 : 4 : 2′ : 4′-*tetrahydroxyarsenobenzene* (annexed formula), the tetrahydrochloride of which formed a dull yellow powder. The solutions gave a precipitate of the free base, soluble in excess, when mixed with sodium hydroxide, carbonate or hydrogen carbonate, but the alkaline solution soon oxidised to indophenol dyes. In hydrochloric acid, the substance gave a pale yellow diazo-solution which yielded a dark red compound with resorcinol, but in acetic acid solution sodium nitrite gave a dark green precipitate which immediately changed to a dark brown, arsenic-free dye of the Bismarck-brown type. Diazotised *p*-nitroaniline also coupled with the compound in alkaline solution, giving an arsenic-free, brownish-red dye. When the hydrochloride was boiled with water, it was hydrolysed, like 2 : 4 : 2′ : 4′-tetra-



aminoarsenobenzene (Karrer, *loc. cit.*), to the known 2 : 4-diaminoresorcinol, which behaves towards nitrous acid in the above curious ways.

4-*Hydroxy*-2-*methoxyphenylarsinic acid*, $C_7H_9O_5As$, was prepared from resorcinol monomethyl ether in colourless crystals, m. p. 209°, and was reduced by hypophosphorous acid and potassium iodide to 4 : 4′-*dihydroxy*-2 : 2′-*dimethoxyarsenobenzene*, a yellow powder. It was also nitrated to 5-*nitro*-4-*hydroxy*-2-*methoxyphenylarsinic acid*,

$$C_7H_8O_7NAs,H_2O,$$

pale yellow scales, m. p. 237°, which was reduced by hyposulphite to the 5-*amino*-compound, $C_7H_{10}O_5NAs,2H_2O$. This yielded the yellow *hydrochloride* of 5 : 5′-*diamino*-4 : 4′-*dihydroxy*-2 : 2′-*dimethoxyarsenobenzene*, which formed the *hydrochloride* of 2-*amino*-5-*methoxyphenol* (4-*aminoresorcyl* 1-*methyl ether*), $NH_2\cdot C_6H_3(OH)\cdot OMe$, colourless needles, decomp. 220°, on boiling with water. This immediately reduces ammoniacal silver solutions, and the yellow diazo-solution gives a deep red dye with resorcinol.

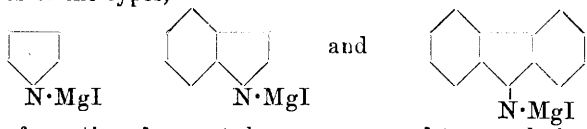
The dimethyl ether of resorcinol yielded 2 : 4-*dimethoxyphenylarsinic acid*, $H_2O_3As\cdot C_6H_3(OMe)_2$, in silky needles, m. p. 242—243°.

J. C. W.

Magnesium Complexes of Pyrrole, Indole, and Carbazole in their Relations to Chlorophyll. V. V. Tschelincev and B. V. Tronov (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1876—1886).—Willstätter's formula for chlorophyll raises a question as to the possibility of the existence of such an organo-magnesium compound in the medium, rich in water, present in the green parts of plants. Further, the comparison which has been made between the assimilation of carbon dioxide by plants and the Grignard reaction renders it necessary to ascertain if this reaction demands such great mobility of the magnesium atom as is incompatible with the stability of chlorophyll towards water. No organo-magnesium compound is as yet known in which the magnesium atom, whether united to carbon, or to hydroxyl, or to an amino-group, exhibits this stability under the influence of water. With the object of casting light on these points, the authors have investigated (1) magnesium complexes of pyrrole, indole, and carbazole and their thermochemical behaviour towards water, and (2) the thermochemistry of the introduction of magnesium into pyrrole and similar nuclei and the capacity of such magnesium derivatives to form complexes.

As regards the action of individual organo-magnesium compounds on amines, Tschelincev (A., 1907, i, 499) showed that tertiary amines give only monoaminic complexes of the type $NR_3I\cdot MgR$, whereas primary and secondary amines, especially those containing aliphatic radicles, yield mono-, di-, and tri-aminic complexes of the forms (with secondary amines), $MgRI,NHR_2$, $MgRI,2NHR_2$, and $MgRI,3NHR_2$; in a second stage of the reaction, these undergo decomposition, with evolution of gas and rise of temperature, into the derivatives described by Meunier (A., 1903, i, 544). At low temperatures, pyrrole, indole and carbazole react with individual organo-magnesium compounds, giving complexes which at the ordinary temperature undergo gradual

transformation, accompanied by evolution of gas, into magnesium derivatives of the types,



This transformation does not, however, proceed to completion, even at 20°, direct determination of the thermal effects accompanying introduction of the magnesium into these compounds being, therefore, impossible. This end was, however, attained indirectly in the following manner. The individual organo-magnesium compound was prepared directly in the calorimetric chamber from methyl iodide and magnesium in benzene, the pyrrole, indole, or carbazole being then added in benzene solution. The product was next heated at 60—70° in order to complete the replacement, and then placed in the calorimeter, where the heat effect of its decomposition by water was measured. The heats of solution of pyrrole, indole, and carbazole in benzene were determined separately, and the heat effect of the decomposition by water of magnesium propyl iodide has been previously determined, whilst the heats of the actions of pyrrole, indole, and carbazole on a mixture of magnesium iodide and hydroxide in water are approximately zero.

The results obtained are as follows. $C_4H_4N\cdot MgI + aq. = C_4H_5N + \frac{1}{2}MgI_2,aq. + \frac{1}{2}Mg(OH)_2 + 40{\cdot}1$ Cal., the corresponding values for indole and carbazole being 42·0 Cal. and 46·7 Cal. respectively. These magnesium derivatives are rapidly decomposed, and are thus highly unstable in presence of water. Since, $MgPrI + aq. = C_3H_8 + \frac{1}{2}MgI_2,aq. + \frac{1}{2}Mg(OH)_2 + 69{\cdot}1$ Cal., it follows that the heat effects of the reaction, $R\cdot NH + MgPrI = R\cdot N\cdot MgI + C_3H_8$, are 29·0, 27·1, and 22·4 Cal. respectively for pyrrole, indole, and carbazole. In the case of carbazole, where the 2-position of the pyrrole nucleus is substituted, no isomerisation can occur, but Oddo's results (A., 1909, i, 672) show that the pyrrole and indole derivatives may undergo isomeric change into magnesium 2-pyrryl and 2-indolyl iodides, and it is difficult to state which forms are yielded by the action of magnesium propyl iodide on pyrrole and indole.

The higher valencies of compounds of the pyrrole series are known to be feeble, and in agreement with this, the action of pyrrole on magnesium pyrryl iodide, that of indole on magnesium indolyl iodide, and that of carbazole on magnesium carbazolyl iodide are found to be accompanied by zero thermal effects. The same is the case with the actions of pyrrole, indole, and carbazole on magnesium ethoxy-iodide, which is a reagent of great sensitiveness towards higher valencies in organic compounds of the most varied types.

The instability of magnesium derivatives of pyrrole, indole, and carbazole does not lend support to Willstätter's formula for chlorophyll (compare Mohr, *Chem. Zeit.*, 1914, **39**, 571). The stability of the magnesium is not explained by combining, as Willstätter suggested, the higher valencies of two pyrrole nuclei with two other pyrrole nuclei, since the nitrogen atoms of pyrrole exhibit only a feeble capacity to form complexes. Willstätter's further suggestion that these two added rings in the chlorophyll molecule exist in an isomeric

form with increased valency raises the question of the non-appearance of the basic properties of the rings when the magnesium is removed from the molecule. T. H. P.

Magnesium Derivatives of Piperidine, Tetrahydroquinoline, and Hydroacridine, and the Theory explaining their Relative Capacities for the Formation of Complexes. V. V. TSCHELINCEV and B. V. TRONOV (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1886—1898).—These investigations were carried out similarly to those on pyrrole, indole, and carbazole (preceding abstract). The formation of the magnesium derivatives by the action of magnesium propyl iodide on these bases in benzene solution commences at about 20°, and was carried to completion at 70°. The heats of solution in benzene are: piperidine, 0·34 Cal.; tetrahydroquinoline, 0·17 Cal.; and hydroacridine, 1·63 Cal., and the actions of the three bases on a mixture of magnesium iodide and hydroxide in water are 5·98, 0·05, and 0 Cal. respectively. Hydroacridine behaves like pyrrole, indole, and carbazole towards organo-magnesium compounds, with which it does not form complexes, but in the case of piperidine and tetrahydroquinoline, such complexes are formed with development of a considerable amount of heat.

The results obtained are as follows: $C_5H_{10}N\cdot MgI + aq. = C_5H_{11}N + \frac{1}{2}MgI_2$, aq. $+ \frac{1}{2}Mg(OH)_2 + 36·4$ Cal., the corresponding heats of reaction for tetrahydroquinoline and hydroacridine being 42·3 Cal. and 48·8 Cal. respectively. Since, $MgPrI + aq. = C_3H_8 + \frac{1}{2}MgI_2$, aq. $+ \frac{1}{2}Mg(OH)_2 + 69·1$ Cal., it follows that $C_5H_{11}N + MgPrI = C_5H_{10}N\cdot MgI +$ 32·7 Cal., the corresponding values for the reactions with tetrahydroquinoline and hydroacridine being 26·8 and 20·3 Cal. The reaction, $C_5H_{10}N\cdot MgI + C_5H_{11}N$ gives 15·34 Cal.; $C_5H_{10}N\cdot MgI, C_5H_{11}N + C_5H_{11}N$, 2·12 Cal.; $C_5H_{10}N\cdot MgI, 2C_5H_{11}N + C_5H_{11}N$, 0·14 Cal.; $C_9H_{10}N\cdot MgI + C_9H_{11}N$, 3·70 Cal.; $C_9H_{10}N\cdot MgI, C_9H_{11}N + C_9H_{11}N$, 1·26 Cal.; $C_9H_{10}N\cdot MgI, 2C_9H_{11}N + C_9H_{11}N$, 0 Cal.; $C_{13}H_{10}N\cdot MgI +$ 1, 2, or 3 $C_{13}H_{11}N$, 0 Cal.

Thus, piperidine gives mono-, di-, and, possibly, tri-amino complexes, tetrahydroquinoline only mono- and di-amino-complexes, and hydroacridine, no complexes at all. The structures of the mono- and di-amino-complexes may be represented, for piperidine, by the formulæ, $C_5H_{10}N\cdot Mg\cdot NHI\cdot C_5H_{10}$ and

$$C_5H_{10}N\cdot Mg\cdot NH(C_5H_{10})\cdot I\cdot NH\cdot C_5H_{10},$$

quinquevalency of the iodine atom being required for the triaminic complex. The formation of complexes with the three bases is in complete agreement with the basic properties of these compounds.

These results indicate that the higher valencies are strongest in piperidine, less marked in tetrahydroquinoline, and absent from pyrrole, indole, carbazole, hydroacridine, furan and thiophen. Such differences seem to depend on the presence or absence of a double linking at the carbon atom in the 1-position to the nitrogen, sulphur or oxygen atom of the nucleus. Thus, piperidine contains no such double linking, tetrahydroquinoline only one, and the remaining bases, two. It is evident that furan and thiophen must be classed in the same group as pyrrole and hydroacridine. T. H. P.

Physiological Chemistry.

The Effect of Dividing the Pulmonary Vagus on Respiration in Dogs. WALTER M. BOOTHBY and V. N. SHAMOFF (*Amer. J. Physiol.*, 1915, **37**, 418—432).—Dogs were kept alive for months after the operation, and the respiration was practically unaltered. The pulmonary vagus transmits no impulses that control functions essential to life. The nerves have no power over the normal regulation of gaseous metabolism, pulmonary ventilation, or the gaseous exchanges in the lungs. W. D. H.

The Action of Intravenous Infusions of Sodium Chloride, Acids and Alkalis on Respiratory Metabolism During Urethane Narcosis. J. C. RAEDER (*Biochem. Zeitsch.*, 1915, **69**, 257—288).—When the narcotisation by urethane has been conducted under suitable conditions, rabbits can be used for two or three days for respiration experiments. The respiratory exchange is then very constant, varying only by about 2% in one or two hours. The secretion by the kidneys is not affected. Sudden intravenous injection of sodium chloride causes an increase in respiratory exchange. The effect of slow, permanent infusions can also be investigated; in this case, the work of the kidneys and heart can be kept constant, and the metabolism remains more stable than is the case when sudden large infusions are made. The infusions of sodium chloride cause an increase in the respiratory exchanges, which soon diminish when the solutions are strong, owing, apparently, to a toxic action on the cells and the high osmotic pressure. There is generally an increased secretion of urine, and the sodium chloride is eliminated in a few hours; the increased work thus entailed on the organism may account for the greater metabolism. Sodium carbonate increases the oxygen uptake; the first action of acids is the same, but after a time the respiratory exchange sinks (intoxication?). Concentrations of $N/5$-sodium hydroxide and $N/6$-hydrochloric acid are so toxic that they cannot be employed for experiments. S. B. S.

The Circulation Rate in Man at Rest and Work. WALTER M. BOOTHBY (*Amer. J. Physiol.*, 1915, **37**, 383—417).—The circulation rate increases proportionally to the oxygen consumption, and the main controlling fact in the regulation of the rate is believed to be the hydrogen ion concentration of the arterial blood; this regulation is one of great delicacy. The rate may be doubled by a rise of total acidity of the blood corresponding with 2 mm. of carbon dioxide. W. D. H.

The Tissue Fluid in Normal and Nephritic Animals. A. E. BOYCOTT and J. S. C. DOUGLAS (*J. Path. Bact.*, 1915, **19**, 528—548).—The normal blood of rabbits contains 0·55, the plasma 0·65, and the corpuscles 0·3% of sodium chloride. After strong

dextrose solution is injected into the blood-vessels, liquid is brought into the blood from the tissues; this fluid contains some protein and about 0·5% of sodium chloride. If sodium sulphate is used instead of dextrose, the fluid which comes into the blood contains 0·35% of sodium chloride; after hæmorrhage, the entering fluid contains from 0·4 to 0·7% or more of sodium chloride. The entering fluid cannot be regarded as tissue fluid, but some differential filtration by the capillary wall must be assumed to take place. In nephritis caused by uranium, the entering fluids in parallel experiments contain more protein and more chlorides than in normal rabbits. This difference probably signifies a difference in the composition of the tissue fluid. W. D. H.

The Effect of Work on the Hæmoglobin and Red Corpuscles of the Blood. Walter M. Boothby and Frank B. Berry (*Amer. J. Physiol.*, 1915, **37**, 378—382).—The hæmoglobin and red corpuscles, and therefore the oxygen-carrying capacity, of a unit volume of blood are increased by work, provided perspiration occurs, but not otherwise. W. D. H.

The Level of the Sugar in the Blood from the Liver under Laboratory Conditions. J. J. R. Macleod and R. G. Pearce (*Proc. Amer. Soc. Biol. Chem.*, 1914; *J. Biol. Chem.*, 1915, **20**, xxiii—xxiv).—The blood from the hepatic vein in dogs was examined at short intervals by Bang's micro-method. For thirty minutes after etherisation, the sugar concentration falls; in four out of six animals the sugar then returned to the normal level, but in the other two the original decline persisted. W. D. H.

The Level of Blood Sugar in the Dog. P. A. Shaffer and R. S. Hubbard (*Proc. Amer. Soc. Biol. Chem.*, 1914; *J. Biol. Chem.*, 1915, **20**, xxxiv).—The normal percentage is 0·05; it rises during anæsthesia to 0·1—0·2; this is due to mild asphyxia, and may be corrected by forced artificial respiration. W. D. H.

Animal Calorimetry. IX. The Influence of Meat Ingestion on the Amino-acid Content of Blood and Muscle. Mary B. Wishart (*J. Biol. Chem.*, 1915, **20**, 535—537).—The ingestion of 1000 grams of meat by the dog increases the amount of amino-acids and urea in the blood; in the muscles this is true for urea, but not for amino-acids. The specific dynamic action of protein is therefore not due to certain amino-acids acting in increased concentration on protoplasm; the cause must be sought in the metabolic processes involved in the transformation of these amino-acids. W. D. H.

Uric Acid Metabolism. I. Uric Acid in the Blood of Ox and Chicken. Stanley R. Benedict (*J. Biol. Chem.*, 1915, **20**, 633—640).—Ox-blood contains 0·5 mg. of free uric acid per 100 c.c. A much larger figure is obtained if substances which interfere with the colour reactions are not removed; in chicken-blood these inter-

fering substances are not so abundant. After boiling with hydrochloric acid, the yield of uric acid rises to 6, or even 7, mg. per 100 c.c. If blood is simply allowed to remain, the combined uric acid gradually falls to zero, and the free uric acid increases; this is attributed to enzymic action; the final figure for the free uric acid is greater than that obtained after the use of hydrochloric acid, probably because that reagent destroys some of the uric acid. The uric acid is present as a very stable combination. The high figure for the total uric acid in an animal that secretes but little in its urine was not finally accepted until the uric acid was isolated and fully identified; the uric acid is wholly contained in the blood-corpuscles. In chicken-blood, the percentage of free uric acid is 4·8 mg.; there is no combined uric acid, and it is practically all in the serum, not in the corpuscles. W. D. H.

The Estimation of Lipoid and Acid-soluble Phosphorus in Small Amounts of Serum. Isidor Greenwald (*J. Biol. Chem.*, 1915, **21**, 29—36).—The method depends on the fact that all lipoid phosphorus is precipitated by a picric–acetic acid mixture. Inorganic phosphorus is left in solution. Phosphorus in protein form is negligible in amount. The amount of inorganic phosphorus in serum varies normally with diet and the stage of digestion from 0·002 to 0·006%, and of lipoid phosphorus from 0·007 to 0·013%. In nephritis there is evidence of retention of inorganic phosphates, and in some cases there is also an increase in the lipoid phosphorus of the serum. W. D. H.

The Activation of Soja Urease by Human Serum. Rudolf Neumann (*Biochem. Zeitsch.*, 1915, **69**, 134—140).—Human serum increases the action of soja urease by about eightfold; no differences could be found in the auxo-reaction with the sera taken from the most varied pathological cases, and the amount of auxo-substance is constant. Fluids from the pleura show the same action. S. B. S.

The Dependence of the Destruction of the Complement on the Presence of Oxygen. Martin Jacoby and Margarete Jacoby (*Biochem. Zeitsch.*, 1915, **69**, 127—133).—It has been found by Jacoby and Schütze that the complement of guinea-pigs' serum is destroyed when shaken at 37°. It is now found that if hydrogen is led through the serum before shaking, and the agitation takes place in the absence of air, the destruction of the complement does not take place. To prevent inactivation, the oxygen must be completely driven out; when once freed from oxygen, the serum is well protected against the shaking action. S. B. S.

Gastro-intestinal Studies. VIII. Estimation of Trypsin in the Gastric Contents. William H. Spencer (*J. Biol. Chem.*, 1915, **21**, 165—167).—In Ehrenreich's method, the gastric contents are neutralised with sodium hydroxide, phenolphthalein being used as indicator; caseinogen is then added, the mixture incubated for

two and a-half hours, and the amount of digestion of the protein ascertained. In the author's hands, this gave bad results; good results were obtained by introducing three chief modifications: (1) sodium hydrogen carbonate is used for neutralising; (2) the quantity of caseinogen added is reduced by half; and (3) incubation is carried out for five hours. W. D. H.

The Rate of Oxidation of Enzymes and their Pro-enzymes. W. E. Burge and E. L. Burge (*Amer. J. Physiol.*, 1915, **37**, 462—470).—A full account of a research already published briefly (this vol., i, 182). The fact that trypsin and pepsin are relatively easy to oxidise makes it possible for the alimentary mucous membrane to protect itself from digestion. W. D. H.

The Distribution of Gastrin in the Body. R. W. Keeton and F. C. Koch (*Amer. J. Physiol.*, 1915, **37**, 481—504).—A full account of a research of which a preliminary notice has already appeared (this vol., i, 190). W. D. H.

Digestive Processes in Limulus. Helen I. Mattill and H. A. Mattill (*Proc. Amer. Soc. Biol. Chem.*, 1914; *J. Biol. Chem.*, 1915, **20**, xxii—xxiii).—The entire tract is alkaline. A reddish fluid is sometimes obtainable from the stomach, and this possesses the same digestive powers as the intestinal contents; a protease, an amylase (forming dextrose from starch), and a lipase are present. W. D. H.

The Influence of Food on Metabolism. Graham Lusk (*Proc. Amer. Soc. Biol. Chem.*, 1914; *J. Biol. Chem.*, 1915, **20**, viii—xvii).—Presidential address, in which the author summarises the results of his numerous researches on this subject. W. D. H.

Animal Calorimetry. XI. The Causes of the Specific Dynamic Action of Foodstuffs. Graham Lusk (*J. Biol. Chem.*, 1915, **20**, 555—617).—After prolonged confinement in a cage without loss of body-weight, a dog may show a marked reduction in basal metabolism; after exercise, this disappears. Ingestion of a cold solution of dextrose causes a discrepancy between the measurement of heat by the direct and indirect methods which may last for three to four hours; the heat production is increased to replace that abstracted by the cold solution. Cold water alone acts in the same way, but to a less extent; it explains certain discrepancies after meat ingestion noted previously: 5·5 grams of glycine increased metabolism 7·3%, 5·5 grams of alanine increased it by 7%. The two together increased it by 18%, which is the same increase noted with 50 grams of dextrose. The increase in metabolism produced by glycine is proportional to the amount ingested, and the extra heat production is nearly equal to its energy content. In the case of alanine, the same occurs, and the extra heat is 53% of its energy content. The extra heat is not proportional to the sugar formed, but there is some evidence that one molecule

of glycollic acid (from glycine) has the same effect as one molecule of lactic acid from alanine. When carbohydrate is converted into fat, there is a small exothermic elimination of heat, for which allowance can be calculated. Glycine or alanine plus sugar produces an increase in metabolism almost as great as the sum of the increases induced when these substances are given alone. In heat production, sucrose and lævulose have less effect than dextrose; galactose causes a slight effect, and lactose none at all. Ethyl glycollate is a poison. Ethyl alcohol increases the level of basal metabolism, and does not merely replace an isodynamic quantity of fat. The effect of dextrose and alcohol together is nearly equal to the sum of the effects each produces alone. It is probable that lactic acid (from ethyl lactate) acts as a stimulus to higher metabolism. Phloridzin in fasting dogs causes an increase in metabolism, which may be 70% over the basal level. Dextrose and lævulose have no influence on the level of heat production in phloridzin glycosuria, but glycine and alanine increase the metabolism of phloridzinised dogs, although they are not oxidised, and their energy content appears as sugar and urea in the urine. Their maximal effect on heat production coincides with the period of their maximal metabolism, and since amino-acids themselves do not stimulate metabolism, as the author thought previously, the conclusion is drawn that the real stimuli are intermediary products, such as glycollic and lactic acids, and thus an explanation is provided of the specific dynamic action of protein. W. D. H.

Animal Calorimetry. X. The Rate at which Ingested Glycine and Alanine are Metabolised. Frank A. Csonka (*J. Biol. Chem.*, 1915, **20**, 539—554).—Phloridzination repeated a second or third time after recovery always leads to a large output of sugar during the first hours. The urinary nitrogen does not increase immediately, and the D : N ratio varies between 5·5 and 17·9, indicating that repeated phloridzination has no effect on the character of the glycosuria induced. The ingestion of 2 grams of Liebig's extract of beef has no effect on the output of sugar by the phloridzinised dog. The rapidity of the absorption and elimination of ingested dextrose by such an animal is almost the same as the absorption of isoglucogenic amounts of glycine or alanine, and of the elimination of the synthetic sugar produced from them after deamination. The amount of extra sugar so eliminated is a better index of the hourly metabolism of these amino-acids when given to a normal dog than the nitrogen output. After giving ethyl lactate to a phloridzinised dog, only 40% of the dextrose which could have arisen appeared in the urine. W. D. H.

Metabolism of Amino-acids in the Organism. III. Action of the Kidneys on Amino-acids added to Circulating Blood or Ringer's Solution. Camillo Artom (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 468—475. Compare Lombroso, this vol., i, 476).—Circulation through the isolated kidneys of blood containing about

0·8% of an amino-acid results in diminution, amounting to as much as 17%, of the content of amino-acid; about 25—50% of the amount thus lost is found unchanged in the kidneys, the remainder being destroyed. Similar results are obtained when the blood is replaced by Ringer's solution. T. H. P.

Metabolism of Amino-acids in the Organism. IV. Action of the Intestine on Amino-acids Added to Circulating Blood or Ringer's Solution. Ugo Lombroso (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 475—482).—The action of the intestine on amino-acids is different from that of the other tissues which have been studied. Blood containing about 0·8% of amino-acid loses about 20% of the latter, and in no cases is an appreciable amount of the amino-acid lost deposited in the tissue, whilst sometimes a certain proportion of the amino-acids of the tissue disappears. In one instance, where the mucus had a high content of amino-acids, 21% of the latter was lost, whereas the blood lost only 18% of its dissolved amino-acids. When the blood is replaced by Ringer's solution, the loss of amino-acids is considerably diminished, and the amount deposited in the tissues increased to such an extent that, in some cases, it counterbalances the amount removed from the liquid. T. H. P.

How are the Plant Proteins of the Diet Utilised in the Animal Body? I. H. Boruttau (*Biochem. Zeitsch.*, 1915, **69**, 225—244).—Dogs were first starved, and then fed on a nitrogen-free diet. During the last days of this diet, the daily excretion of nitrogen in the urine was estimated. A period was then interposed when, in addition to the nitrogen-free constituents (which were sufficient for the caloric needs of the organism), a protein of known nitrogen content was given. This period was followed by the nitrogen-free diet. The physiological value of the protein was calculated from the two following formulæ:

$$100 \cdot \frac{\text{Urine-nitrogen on } N\text{-free diet} + \text{nitrogen balance}}{\text{Ingested nitrogen}}$$

or

$$100 \cdot \frac{\text{Urine-nitrogen on } N\text{-free diet} + \text{nitrogen of fæces} + \text{balance}}{\text{Ingested nitrogen}}$$

The urine nitrogen was taken as the average excreted daily before and after the period with the super-added protein. The nitrogen balance in the above formulæ is that during the period of protein ingestion. For nitrogen in white bread, the values found were 46·5 and 50·45%, and for gliadin alone 37 and 40%. For meat the numbers were 108·7 and 112·2. Spinach nitrogen gave values 67·2 and 76·6. The addition of a small amount of spinach to gliadin caused considerable increase in the food value (up to 47·1 and 54·8%), and oat-straw, which contained very little nitrogen, increased it to about 60%. The general conclusion is drawn that the physiological food-value of the proteins is higher than is indicated by the experiments on the pure proteins, and that if the

natural conditions are imitated more, and certain accessory substances which are contained in the husks and the cuticular formations of plants are added, much higher food-values are attained.

S. B. S.

Gastro-intestinal Studies. VII. Utilisation of Ingested Protein as Influenced by Under-mastication (Bolting) and Over-mastication (Fletcherising). L. F. Foster and P. B. Hawk (*J. Amer. Chem. Soc.*, 1915, **37**, 1347—1361).—Experiments are described in which normal men were fed on a fairly high nitrogen diet. They were divided into four periods: (1) preliminary, in which the food was consumed in a normal manner; (2) in which it was swallowed without proper mastication; (3) in which it was over-masticated, or "fletcherised"; and (4) in which a return was made to the normal method of eating. The nitrogen was estimated in the fæces and urine.

It was found that the proteins were utilised to the greatest extent when the food was fletcherised, and least when it was bolted, but in the former case the utilisation was only 0·17% higher than during the period of normal mastication. The thorough mastication of starchy foods should be encouraged, so as to ensure salivary digestion, but with regard to the utilisation of protein, the results of the present investigation do not show any necessity for excessive mastication, nor do they indicate that under-mastication is harmful.

E. G.

Nutrition with Purified Food-substances. E. V. McCollum and Marguerite Davis (*J. Biol. Chem.*, 1915, **20**, 641—658).—Although the authors place due weight on the kind of protein given, and more especially on the value of the sort of fat administered (some of which they do not pretend are absolutely purified), they put forward experiments to show that, on a synthetic diet, rats can be made to grow and live healthily; the whole trend of their paper is against the existence of problematical vitamines. An important factor is the vitality of the animals used; many rats will die, others will live but not grow, others, again, will live, grow, and breed. If this stronger stock is selected, the good results named can be obtained.

W. D. H.

The Influence of Certain Vegetable Fats on Growth. E. V. McCollum and Marguerite Davis (*J. Biol. Chem.*, 1915, **21**, 179—182).—In rats, the absence of fat in a synthetic diet stops growth; certain fats promote growth (butter-fat, cod-liver oil, etc.); others (lard, tallow, etc.) do not. It is now shown that fats from maize, wheat, rye, and oats fall into the former category, but many plant fats do not.

W. D. H.

Starvation and Obesity, with Special Reference to Acidosis. Otto Folin and W. Denis (*J. Biol. Chem.*, 1915, **21**, 183—192).—Obesity is not a predisposing cause or contributing factor in the onset or intensity of acidosis in starvation. The

total amount of acetone excreted with the breath in starvation is insignificant (at most 1 gram a day); clinical statements to the contrary are exaggerations. By repeated fasts of moderate duration, the obese acquire an increased ability to starve without the production of acetone substances. The obese lose less body-protein than others in fasts of four to six days, and with repetition the loss becomes still smaller. Fasting for moderate periods is a safe and effective method for reducing the weight in obesity. W. D. H.

Dextrose Content of Hen's Eggs. M. E. PENNINGTON, N. HENDRIKSEN, E. L. CONNOLLY, and B. M. HENDRIX (*Proc. Amer. Soc. Biol. Chem.*, 1914; *J. Biol. Chem.*, 1915, **20**, xxi).—In the white the percentage varies from 0·3 to 0·6, and in the yolk from 0·08 to 0·24. During the incubation of fertile eggs, the amount falls, but is unaffected in non-fertile eggs. The amount in commercial frozen eggs averages 0·34%. When decomposition sets in, the sugar gradually disappears. W. D. H.

The Cholesterol Metabolism of the Hen's Egg During Incubation. J. HOWARD MUELLER (*J. Biol. Chem.*, 1915, **21**, 23—28).—In the new-laid egg, the cholesterol is free. After the thirteenth day of incubation, gradual esterification takes place, until, at the time of hatching, 40% of the cholesterol is in ester-form. This may indicate a detoxifying action, harmless esters being formed with toxic fatty acids liberated from lecithin during the later stage of embryonic development. W. D. H.

The Relative Effects of Weak and Strong Bases on the Rate of Oxidations in Sea Urchin's Eggs. JACQUES LOEB and HARDOLPH WASTENEYS (*J. Biol. Chem.*, 1915, **21**, 153—158).—The oxidations induced by sodium hydroxide occur at the surface of the egg (Warburg). A comparison of the rate of oxidation induced by strong and weak bases shows that oxidation occurs chiefly at the surface, and thus but little oxygen enters the deeper parts of the cell, but the layers adjacent to the surface are also seats of oxidation. W. D. H.

The Hepatic Fatty Infiltration in Late Pregnancy and Early Lactation. V. H. MOTTRAM (*Proc. Amer. Soc. Biol. Chem.*, 1914; *J. Biol. Chem.*, 1915, **20**, xxxi).—In these conditions the liver-fat increases in cats and rabbits. From iodine values, the conclusion is drawn that the liver is infiltrated with fatty acid. W. D. H.

The Lipoids of Ancient Egyptian Brains and the Nature of Cholesteryl Esters. A. LAPWORTH and F. A. ROYLE (*J. Path. Bact.*, 1915, **19**, 474—477).—The existence of only one series of esters of cholesterol and fatty acids was established. The chlorides of the higher fatty acids, when heated with cholesterol at moderate temperatures, yield esters; above 350° they give aliphatic ketones. The cholesterol of ancient Egyptian brains is

present mainly in the form of esters, as stated by Mair. No appreciable quantity of higher fatty ketones was found in them. W. D. H.

The Urea Content of Human Cerebro-spinal Fluid and Blood. G. E. Cullen and A. W. M. Ellis (*J. Biol. Chem.*, 1915, **20**, 511—512).—The results show that animal tissues, in general, are osmotically permeable to urea, which tends to reach the same concentration in the different body-fluids. W. D. H.

Acceleration of Liver Autolysis. H. C. Bradley (*Proc. Amer. Soc. Biol. Chem.*, 1914; *J. Biol. Chem.*, 1915, **20**, xxix—xxx).—Liver autolyses until 25% of the nitrogen is not precipitated by tannic acid; this takes ten days. Hydrochloric acid (1/50 mol.), manganese chloride (1/10 mol.), peptone, caseinogen, and boiled liver accelerate it. Egg-albumin and edestin have no effect. The normal liver contains three protein groups: (1) from the connective tissues, which are not attacked by proteases; (2) hæmoglobin and albumin, which are autolysed only when the accelerating agents are added; and (3) globulins, which are readily and completely autolysed. W. D. H.

Autolysis. I. The Accelerating Effect of Manganous Chloride on Liver Autolysis. H. C. Bradley and Max Morse (*J. Biol. Chem.*, 1915, **21**, 209—221).—In the presence of excess of water, 75% of the nitrogen is undigested during the autolysis of pig and dog livers. If manganous chloride is added, this figure is reduced to 10—25%; the connective tissue, which remains indefinitely undigested, accounts for 10%. Beyond 1/10 mol., manganous chloride diminishes the speed of autolysis. The salt is believed to alter the resistant fraction of the liver proteins so as to render them digestible by the protease present. W. D. H.

The Fatty Substances in the Liver of Selachians (Amyliobatis aquila). Raffaele Paladino (*Biochem. Zeitsch.* 1915, **69**, 192—198).—The fat in the liver of *Amyliobatis aquila* has m. p. 50°, and solidifying point 20°. It gives two absorption bands between C and D. Acid number, 10·2; saponification number, 193·8; Reichert-Meissl number, 2·66; and the iodine number, 104·8. The fatty acids consist of oleic, palmitic, and stearic acids. The fat contains phosphorus and iron. S. B. S.

Detoxicating Effect of the Liver of Cathartes Aura (Turkey Buzzard) on β-Amino-4-ethylglyoxaline. Allan C. Eustis (*Biochem. Bull.*, 1915, **4**, 97—99).—The animal named was chosen in view of its fondness for carrion; it is also known that the liver exerts a detoxicating action on intestinal toxins. Incubation of the sterile surviving liver with β-amino-4-ethylglyoxaline, a very potent poison, destroyed its activity entirely. Boiling the liver inhibits its detoxicating power. W. D. H.

Does the Cholesterol-content of the Diet Exert any Influence on the Cholesterol Excretion of the Bile? L. D'AMATO (*Biochem. Zeitsch.*, 1915, **69**, 217—224).—If a diet rich in lipoids is administered to a dog with a biliary fistula, this causes only an infinitesimally small increase of the cholesterol and salts of the bile. The increase is so small that the statements are not justified that the bile is its chief channel of excretion for the organism, and that the cholesterol is, for the most part, converted into cholic acid, and excreted thus in the form of bile salts. S. B. S.

The Presence of Iodine in the Human Fœtal Thyroid Gland. FREDERIC FENGER (*J. Biol. Chem.*, 1915, **20**, 695—696).—Both enlarged and normal fœtal thyroids contain iodine, at least during the last three months of intra-uterine life; the normal glands contain more iodine and less phosphorus than enlarged glands. These conditions in man are analogous to those existing in cattle, pigs, and sheep. W. D. H.

Reproduction in the Domestic Fowl. XIII. The Failure of Extract of the Pituitary Gland (Anterior Lobe) to Activate the Resting Ovary. RAYMOND PEARL and FRANK M. SURFACE (*J Biol. Chem.*, 1915, **21**, 95—101).—If the substance of the anterior lobe of the cow's pituitary gland is injected into the abdominal cavity of hens, no activation of the resting ovary, that is, no induction of ovulation, takes place. W. D. H.

Specific Heat of Muscle Protein and its Relation to the Heat of Combustion. OTTO KRUMMACHER (*Zeitsch. Biol.*, 1915, **65**, 355—364).—The specific heat of dried muscle is 0·265, and of the dried and fat-free muscle 0·257. The determination of this value enables the variation of the heat of combustion of muscle protein with the temperature to be calculated. It is found that the heat of combustion falls 0·428 cal. per 1 gram of muscle protein for one degree rise of temperature. Since the heat of combustion is usually estimated at about 20° below body-temperature, the physiological heat of combustion of muscle protein is about $20 \times 0{\cdot}428$, or 8·6 cal. below the usually accepted value, which is equivalent to an error of about 0·15%. H. W. B.

Permeability of the Internal Cytoplasm of Animal and Plant Cells. G. L. KITE (*Amer. J. Physiol.*, 1915, **37**, 282—299).—In previous work, the whole emphasis has been placed on the properties of the plasmatic membrane, but it is possible to study permeability in the interior of living cells. The whole protoplasm offers a barrier to the penetration of dyes. Differences in this respect vary with the reagent and the cell employed, and the plasmatic membrane theory is regarded as unsound. W. D. H.

The Active Principles of Different Organs as shown in Kymograph Tracings. GEORGE G. FAWCETT, JOHN ROGERS, JESSIE M. RABE, and S. P. BEEBE (*Amer. J. Physiol.*, 1915, **37**, 453—461).—The term residue is used for that part of the aqueous extract of

an organ which is left after the removal of nucleo-proteins, globulins, and coagulable proteins. The "residue" is the only portion of the extract of thyroid, liver, and pancreas which depresses the arterial blood-pressure. All the organs used contain a depressor substance in the residue, except the adrenal; the activity varies with the nitrogen content. In the case of the thyroid, the depressor substance contains iodine, and the activity is proportional to the iodine content. The depressor agent is not choline, nor is it Popielski's vaso-dilatin. W. D. H.

The Constituents of Animal Fats. J. KLIMONT and K. MAYER (*Monatsh.*, 1915, **36**, 281—287. Compare Klimont and Meisels, A., 1909, ii, 597; Klimont, A., 1912, ii, 580).—The acid mixture isolated from goose-fat (Klimont and Meisels, *loc. cit.*) is not a eutectic of stearic and palmitic acids, as at first believed.

The solid constituents were separated from the crude fat and purified by recrystallisation until the mixture had m. p. 59—60°. The product was then hydrolysed with alcoholic potassium hydroxide, and the component acids were separated by the method used by Meyer and Beer (A., 1912, ii, 593). The main constituents of the acid mixture were margaric and palmitic acids, with a little stearic acid and heptadecoic acid; oleic and linoleic acids could also be detected. It appears probable that the fatty compound, m. p. 60·5°, present in goose-fat is a mixed glyceride, most likely dipalmitomargarin, $C_{16}H_{33}\cdot CO_2\cdot C_3H_5(CO_2\cdot C_{15}H_{31})_2$.

D. F. T.

The Content and Biological Significance of the Fat of Fish and its Variations with the Age of the Individual. OSW. POLIMANTI (*Biochem. Zeitsch.*, 1915, **69**, 145—154).—Further analyses are given which confirm the hypothesis of the author that there is a relationship between the fat-content and the habitat of fishes, the bodies of those which live at the surface of water containing a larger amount of fat than the bodies of those living in deep water or in the sand. A change in fat-content is also found in the same individual at different stages of its existence which corresponds with a change in the habitat; thus, in the cases of *Crenilabras* and *Magil*, the young individual lives mostly at the surface, and the bodies contain a larger amount of fat than is found in the older individuals which live more in the depths. The reverse of this is the case with other species of fish, and in other cases, again, when there is no difference of habitat as regards the depth of the sea inhabited, there is no marked difference in the fat-content of the bodies of the young and older individuals. S. B. S.

Perca-globulin. OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1915, **21**, 193—194).—This protein was first described by Mörner (A., 1904, i, 356; 1909, ii, 329) in the eggs, and especially in the viscous fluid surrounding the eggs, of the common perch (*P. fluviatilis*). It is absent in the sea perch, and in the roe of any

fish examined by Mörner. In the present paper, it is shown to be present in two American perches (*P. flavescens* and *P. sorzoscedion*), and can be most readily identified by its peculiar astringent taste. W. D. H.

The Protein of Honey is Derived from the Bee (Langer) and not from the Pollen (Küstenmacher). Joseph Langer (*Biochem. Zeitsch.*, 1915, **69**, 141—144).—The author has never succeeded in obtaining precipitins by mixing various antisera of high value produced from honey proteins with extracts of pollen; negative results were also obtained when antisera of high value from various descriptions of pollen were mixed with proteins of honey. From these results, the conclusion is drawn that the honey and pollen proteins are different, and contain no protein molecule in common which can serve as an antigen to give rise, after injection, to a serum which produces homologous precipitins. S. B. S.

The Catalase of the Lower Animals. Rudolf Zieger (*Biochem. Zeitsch.*, 1915, **69**, 39—110).—For investigation of the catalase with invertebrate animals, the method of Steche and Waentig was employed. No definite relationship between the mode of life of the organism and its catalase content could be discovered; neither respiration, nutrition, or movement appeared to affect definitely this factor. In the following points, some relationship between the catalase content and the metabolism could be, however, established: (1) The more active organs, such as the liver and kidneys, contain a larger amount of the ferment than the less active organs. (2) The catalase content of the intestines of echinoderms, earthworm, and snails is less in winter, during diminished activity, than it is during summer. (3) Unripe ova have great catalase activity, whereas ripe ova are inactive. The conditions in the case of insects are characteristic. Animals with hemimetabolic development show no differences between the adult and adolescent organisms. In the holometabolic groups (lepidoptera), the youngest larval stages are very active; the catalase content then sinks, and reaches a minimum before the last moulting; it then increases, reaches a maximum in the pappa stage, and then falls rapidly towards the imago stage. S. B. S.

Osmotic Equilibrium between Blood and Milk. F. H. van der Laan (*Chem. Weekblad*, 1915, **12**, 522—541).—A number of determinations of the freezing point of milk and blood, from the results of which the author infers that the freezing point of a sample of milk is identical with that of the blood of the animal from which the milk was derived. A. J. W.

Human Milk. Alfred W. Bosworth (*J. Biol. Chem.*, 1915, **20**, 707—709).—The milk is separated into two portions by a clay filter, the serum and the unfilterable part, which contains the

substances present in the form of an emulsion or as a colloid. The acidity of the serum is the same as that of the original milk; it is due to acid phosphates, and from 3 to 6 c.c. of decinormal alkali are required to make 100 c.c. neutral to phenolphthalein; this is practically the same as in cow's milk; the high figures for the cow given by others are due to the interference of neutral calcium phosphate ($CaHPO_4$). The practice of adding lime-water to cow's milk for infant feeding has therefore no foundation. The following is offered as representing the condition in which the constituents of human milk are present: fat, 3·3; lactose, 6·5; proteins combined with calcium, 1·5; calcium chloride, 0·06; monopotassium phosphate (KH_2PO_4), 0·07; sodium citrate, 0·055; potassium citrate, 0·1; monomagnesium phosphate, 0·027.

W. D. H.

Does Butter-fat Contain Nitrogen or Phosphorus? Thomas B. Osborne and Alfred J. Wakeman (*J. Biol. Chem.*, 1915, **21**, 91—94).—The superiority of butter in promoting growth over lard and some other fats led to the investigation. Nitrogen is absent, or present only in negligible traces. The same is true for phosphorus. About one-half of butter-fat can be separated out as solid fraction; this entirely lacks the growth-promoting property: that resides in the soluble liquid fraction—butter-oil; the amount of phosphorus in this is in the fourth place of decimals, or about one-sixth of that in the entire fat. The contamination with nitrogen or phosphorus is regarded as due to slight admixture with butter-milk. W. D. H.

Variations in Acidity of Human Urine During and After a Seven Day Fast. F. D. Zeman, Jerome Kohn, and Paul E. Howe (*Proc. Amer. Soc. Biol. Chem.*, 1914; *J. Biol. Chem.*, 1915, **20**, xxvi—xxvii).—The acidity varied from an acid urine (P_H 5·1) on the third day of the fast to an alkaline urine (P_H 8) on the last day of the final period of ordinary diet. In the absence of exogenous phosphorus (fasting period), the acidity (true and titratable), phosphates, acetone, acetoacetic acid, and total nitrogen vary together. In the period of non-protein food which followed, the hydrogen ion concentration rose without any increase in urinary nitrogen; acetone and acetoacetic acid were absent. In fasting, the ammonia and β-hydroxybutyric acid increase. Low ammonia excretion is characteristic of recuperation during the final period of ordinary diet, and indicates retention of nitrogen. In the early days of fasting, the excretion of nitrogen rises; this is probably related to the metabolic processes which lead to the excretion of acetoacetic acid. W. D. H.

The Excretion of Creatine During a Fast. F. W. Zeman and Paul E. Howe (*Proc. Amer. Soc. Biol. Chem.*, 1914; *J. Biol. Chem.*, 1915. **20**, xviii).—Acetone and acetoacetic acid interfere with the Folin method of estimation of creatine. When these are removed by Graham and Poulton's method, creatine is found to be present in the urine of fasting persons. W. D. H.

The Influence of Protein Feeding on the Elimination of Creatine in Starvation. WILLIAM C. ROSE (*Proc. Amer. Soc. Biol. Chem.*, 1914; *J. Biol. Chem.*, 1915, **20**, xix).—A rich protein diet in dogs deprived of the pancreas does not cause urinary creatine to disappear. The creatine elimination in starvation is diminished by giving large amounts of protein. In human diabetes, protein feeding has no effect on the output of creatine. This confirms the views of Benedict and Osterberg, and shows that the disappearance of creatine alluded to is due to the carbohydrate arising from protein in metabolism. W. D. H.

Lævulose in Urine. ED. JUSTIN-MUELLER (*J. Pharm. Chim.*, 1915, [vii], **11**, 218—219).—Lævulose has only occasionally been found in urine. In the present case, the lævulose seems to have been derived from raisins and figs which had been consumed in excessive amounts, causing indigestion. N. H. J. M.

The Neutral Sulphur and Colloidal Nitrogen Tests in Cancer. FREDERIC G. GOODRIDGE and MAX KAHN (*Biochem. Bull.*, 1915, **4**, 118—126).—Positive results with either the colloidal nitrogen test or the neutral sulphur test alone are not indicative of carcinoma. Positive results with both tests are, however, strongly indicative of malignancy. W. D. H.

Serum Diagnosis of Rous's Chicken Sarcoma Based on Chemical Methods. CASIMIR FUNK (*Biochem. Bull.*, 1915, **4**, 24—29).—In chickens and rats, the serum from animals with tumours shows a decrease in the precipitate produced by alcohol, and a rise in the nitrogen and phosphorus of the filtrate. W. D. H.

The Relationship between Lactic Acid and Carbohydrate Metabolism. III. Formation of Lactic Acid in Human Diabetes. OTTO VON FÜRTH (*Biochem. Zeitsch.*, 1915, **69**, 199—216).—An investigation was made of the post-mortal formation of lactic acid in the muscular tissue of normal, cachetic, and diabetic individuals. It was found that the excess amount of sugar found in the organs of the diabetic individuals did not lead to the formation of a large excess of lactic acid, and from this fact the conclusion is drawn that the degradation of sugar is not stopped at the stage of formation of lactic acid. On the other hand, the disturbance of metabolism in diabetes appears to exert the tendency to diminish the formation of lactic acid by the muscular tissue (but not by the liver). This tendency is not, however, exhibited in every case. S. B. S.

The Influence of Sodium Carbonate on Glycosuria, Hyperglycæmia, and the Respiratory Metabolism of Depancreatised Dogs. B. KRAMER and J. R. MURLIN (*Proc. Amer. Soc. Biol. Chem.*, 1914; *J. Biol. Chem.*, 1915, **20**, xxvii—xxviii).—The effect is to lower the D : N ratio, the output of sugar, and the amount of

blood sugar. If sugar is given as well as the carbonate, the dextrose is retained, but not as glycogen in liver or muscles; it is not excreted into the alimentary tract, nor does it undergo condensation; the urine contains no lactic acid; the respiratory quotient indicates that only a minimal amount of dextrose is burnt in the body. W. D. H.

The Influence of Calcium Salts on Phloridzin Diabetes. Martin Jacoby and Rudolf A. P. Rosenfeld (*Biochem. Zeitsch.*, 1915, **69**, 155—161).—It has been found by Jacoby, Schroth and Eisner that calcium salts depress the functions of the liver. To test this statement further, the effect of administration of calcium salts to starving dogs with phloridzin diabetes was determined. The nitrogen, dextrose, and acetone substances in the urine were estimated. It was found that the administration of calcium in the above-mentioned circumstances rapidly leads to a diminished nitrogen and sugar output, and also to a diminution in the dextrose: nitrogen ratios. S. B. S.

Theory of Diabetes. V. Narcotic Drugs in Phloridzin Diabetes. W. D. Sansum and R. T. Woodyatt (*J. Biol. Chem.*, 1915, **21**, 1—21).—Dogs were prepared: (*A*) by fasting and injections of phloridzin until the D : N ratio became constant; and (*B*) by the same method plus subcutaneous injections of adrenaline. It is only by the second method that all glycogen is removed from the body. In the *A*-dogs, ether or nitrous oxide causes excretion of extra sugar, but not in the *B*-dogs; the sugar, therefore, comes from glycogen. The *A*-method has been mainly used by previous observers, and their conclusions that various substances thus produce the extra sugar is therefore not well founded. An after-result of narcosis, especially that produced by chloroform, is a decrease in the excretion of nitrogen, sugar, and acetone substances; this is due to a metabolic upset produced by tissue injuries, œdema, asphyxia, and acidosis. Acetaldehyde in *B*-dogs causes no new formation of sugar from fat or other sources. The hypothesis that antiketogenesis and diabetic phenomena depend on the occurrence or non-occurrence of glucoside unions between aldehyde and alcohol groups is untenable. W. D. H.

The Factors of Acid Secretion in Nephritis. Lawrence J. Henderson and Walter W. Palmer (*J. Biol. Chem.*, 1915, **21**, 37—55).—The cases examined fall into two groups: (1) the urinary volume and acidity are high, but the total acid secretion is much diminished; the latter is a sign of acidosis, and is due to a deficit in the urinary ammonia; (2) the urinary volume is about normal, the acidity high, the total acid secretion low or normal, the variations being due to fluctuations in urinary ammonia; these cases involve less acidosis than those in the first group, and are, as a rule, milder. W. D. H.

Retention of Alkali in Nephritis. Lawrence J. Henderson and Walter W. Palmer (*J. Biol. Chem.*, 1915, **21**, 57).—In cases of

nephritis where the urinary ammonia is low, there is retention of alkali after giving sodium hydrogen carbonate; this usually occurs also in the milder cases. This points to an invariable association of acidosis with one type of nephritis, and a frequent association in the other type. W. D. H.

The Effect of Administration of Acid on Parathyroid Tetany. D. WRIGHT WILSON, THORNTON STEARNS, and J. H. JANNEY, Jr. (*J. Biol. Chem.*, 1915, **21**, 169—177).—In dogs the intravenous injections of dilute hydrochloric acid relieved the tetany. It may also be given by the mouth with the same result, but, as a rule, it is not retained by the stomach. This suggests that the benefit is due to a variation in the acid-base equilibrium of the body, and thus offers a new point of view of the causation of the condition. W. D. H.

Experimental Oedema in Frogs. ARTHUR RUSSELL MOORE (*Amer. J. Physiol.*, 1915, **37**, 220—229).—In the normal frog, water which is continually absorbed through the skin is removed by the veins and lymphatics. When a limb is ligatured, liquid accumulates rapidly below the ligature, which consists of transudation from the blood, and water absorbed through the skin, and cannot be removed because of the occluded vessels. The lymph becomes more dilute, and the muscles swell by osmosis. Theories involving acid formation in the tissues, enabling them to take up water, are unnecessary. W. D. H.

Urinary and Serum [Reactions] in Tuberculosis. J. BRONFENBRENNER, J. ROCKMAN, and W. J. MITCHELL, Jr. (*Biochem Bull.*, 1915, **4**, 80—85).—The diazo-, or Weiss, test is less constant than the serum reaction; positive results are only of value if typhoid is excluded, and possibly other pathological states must be excluded also. The urinary reactions in tuberculosis are probably of little or no diagnostic value. In advanced tuberculosis, the "neutral sulphur" of the urine is increased, and this may be of prognostic value. W. D. H.

The Rôle of Serum Antitrypsin in the Abderhalden Tests. J. BRONFENBRENNER, W. J. MITCHELL, Jr., and PAUL TITUS (*Biochem. Bull.*, 1915, **4**, 86).—The appearance of dialysable cleavage products in serum may be produced by non-specific mechanisms, and auto-digestion occurs provided antitrypsin is removed first. W. D. H.

The Nature of the Abderhalden Reaction. J. BRONFENBRENNER (*Biochem. Bull.*, 1915, **4**, 87—89).—The reaction does not depend on the presence of specific enzymes, but on the presence in the blood of pregnancy of the specific anti-substance, which combines with placenta antigen; this sets free the only protease which is present in all serum. It is not the substrate, but the serum itself, which is digested in the Abderhalden test.

W. D. H.

The Relation of Hydrochloric Acid to the Morphological Changes Induced by Chloroform. EVARTS A. GRAHAM (*Proc. Amer. Soc. Biol. Chem.*, 1914; *J. Biol. Chem.*, 1915, **20**, xxv—xxvi).—Necrosis of the liver occurs, not only in "late chloroform poisoning," but can be experimentally produced by other aliphatic halogen-substituted compounds; the effect is held to depend mainly on the action of the respective halogen acids liberated when these substances decompose in the body, for instance, hydrochloric acid from chloroform. The administration of hydrochloric acid produces the effect, and can be inhibited by alkali. Chloral hydrate or ether does not cause the effect. W. D. H.

Acetylation Processes in the Animal Organism. II. Influence of Acetic, Pyruvic, and Acetoacetic Acids on the Formation of *p*-Acetylaminobenzoic Acid. MARIE HENSEL (*Zeitsch. physiol. Chem.*, 1915, **93**, 401—431. Compare Ellinger and Hensel, A., 1914, i, 905).—The addition of sodium acetate to *p*-aminobenzoic acid administered to rabbits results in an increased output of *p*-acetylaminobenzoic acid from the urine. Pyruvic and acetoacetic acids have a similar action, and the author draws the conclusion that these acids are transformed in the body to acetic acid before they are eliminated, in combination with *p*-aminobenzoic acid, in the urine. Evidence for a similar change of acetaldehyde into acetic acid in the body was not obtained. The addition of any of these acids to *p*-aminobenzaldehyde does not lead to any definite increase in the output of *p*-acetylaminobenzoic acid from the urine. H. W. B.

The Effects of Epinephrin (Adrenaline) Infusion on Vaso-motor Irritability. R. G. HOSKINS and WALTER N. ROWLEY (*Amer. J. Physiol.*, 1915, **37**, 471—480. Compare this vol., i, 192).—No satisfactory evidence was obtained that adrenaline increases the irritability of vaso-motor nerves (sciatic and splanchnic of dogs). In most cases it was lessened. Circulating adrenaline is not regarded as a factor in the ordinary processes of an animal's functions. W. D. H.

Action of *dl*-Glyceraldehyde. R. T. WOODYATT (*Proc. Amer. Soc. Biol. Chem.*, 1914; *J. Biol. Chem.*, 1915, **20**, xxiii).—This substance, if given in low dilution, is completely converted into dextrose in the diabetic organism. If given in high concentration, it is apparently burnt. By the mouth, 1·7 grams per kilo. of body-weight causes diarrhœa and suppression of urine; the unchanged triose is found in the fæces; 2·5 grams given under the skin are fatal, but cause no diarrhœa or excretion of unchanged triose by any channel. W. D. H.

A Method for Determining and Comparing the Local Toxicity of Chemical Compounds. H. J. COOPER (*Proc. Amer. Soc. Biol. Chem.*, 1914; *J. Biol. Chem.*, 1915, **20**, xxi—xxii).—The substances investigated were various copper amino-acid compounds.

A small quantity is intracutaneously injected on one side of an animal, and a corresponding amount of another substance on the opposite side. The extent and type of tissue change are then compared. A copper amino-acid mixture prepared from hydrolysed egg-white did not differ greatly in its action from that of copper sulphate, except that the lesion produced by the former was hæmorrhagic, whilst the latter produced a simple necrosis.

W. D. H.

The Absence of Morphine from the Liver in a Case of Chronic Laudanum Addiction. JACOB ROSENBLOOM (*Biochem. Bull.*, 1915, **4**, 90—93).—The absence of morphine from the liver of the case in question indicates that the alkaloid was so changed in the organism as to make it unrecognisable, and that this is marked in cases of habituation to the drug. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Benzene Bacteria. Richard Wagner (*Bied. Zentr.*, 1915, **44**, 212—215; from *Zeitsch. Gärungsphysiol*, 1914, **4**, 289).—From soil, dust, and animal excrementitious matter, seven kinds of bacteria were obtained which are able to utilise benzene derivatives as only source of carbon, phenol and phloroglucinol being oxidised to carbon dioxide, benzene to fatty acids and carbon dioxide, whilst catechol is oxidised, probably to hydroxyquinol. Toluene, xylene, and guaiacol were decomposed, whilst alkaloids and terpenes (except menthol) were not.

The benzene bacteria grow on almost all the usual nutritive solutions, organic acids, and even hydrocarbons, such as light petroleum and petrol.

Some widely distributed bacteria fail to grow in organic nutritive solutions in presence of phenol, whilst in complete nutritive solutions they will grow when a good deal of phenol is present.

Phenols are more readily attacked than benzene. The growth-limits of the bacteria with phenol, catechol, and phloroglucinol were in solutions containing 0·06, 0·075, and 0·04% respectively. Benzene added at the rate of twelve drops per 100 c.c. was completely decomposed.

Resorcinol, pyrogallol, tannin, aniline, naphthalene, and anthracene were not decomposed. N. H. J. M.

Light Production by Luminous Bacteria. E. Newton Harvey (*Amer. J. Physiol.*, 1915, **37**, 230—239).—The dried bacteria will phosphoresce on the addition of water which contains oxygen, although most of them are killed by the drying; oxygen-free water

has no such effect. If the bacteria are ground up with sand, they no longer phosphoresce; hence the phenomenon depends on the integrity of some structure in the cells; ether and toluene do not destroy the photogen, but these reagents in oxygenated sea-water stop phosphorescence. Oxygenated distilled water has the same effect, because the cells are cytolysed. Extraction with cold alcohol does not destroy the power to phosphoresce, but boiling alcohol, cold acetone, and ethyl butyrate do. W. D. H.

Favourable Action Exercised by Manganese on Acetic Fermentation. GABRIEL BERTRAND and ROBERT SAZERAC (*Ann. Inst. Pasteur*, 1915, **29**, 178—181).—Production of acetic acid by *Mycoderma aceti* is considerably increased by manganese sulphate when the solution contains about 25 parts of manganese per million. The acceleration increases with the amount of manganese sulphate until the maximum is reached, and then decreases. N. H. J. M.

The Physical Chemistry of intra-vitam Staining. J. TRAUBE (*Biochem. Zeitsch.*, 1915, **69**, 309—312).—A criticism of certain statements of Höber (this vol., i, 348), especially with reference to the relationship between the surface tension and toxicity, and the action of drugs on protozoa and bacteria, and their behaviour in an electric field. S. B. S.

The Inhibitory Action of Hydrogen Ions on Fermentation. ERIK HÄGGLUND (*Biochem. Zeitsch.*, 1915, **69**, 181—191).—The rate of fermentation with a yeast R'XII was measured in the usual manner in the presence of varying concentrations of lactic acid. The inhibition by the acid of the rate (calculated as relative rates after two days) was found to be directly proportional to the hydrion concentration. Above 35° (and up to 40°), the inhibitory action of the acid increased. S. B. S.

Surface Tension and Ferment Action. E. BEARD and W. CRAMER (*Proc. Roy. Soc.*, 1915, [*B*], **88**, 575—583).—The action of invertase on sucrose is retarded by increasing the surface of the system, owing, in part, to the surface active ferment being driven to the surface, and so prevented from combining with the surface inactive sucrose. It is uncertain whether the retardation is a surface concentration effect only, or whether surface tension also acts by retarding the chemical process taking place in the substrate, that is, the second phase of ferment action.

Indications were obtained that other ferments show retardation by surface tension. When, however, the substrate itself is surface active, the conditions will differ from those where the substrate is surface inactive. N. H. J. M.

Protein Changes in Yeast. II. The Influence of the Medium on Protein Degradation. W. ZALESKI and W. SCHATALOFF (*Biochem. Zeitsch.*, 1915, **69**, 291—304).—Alcohols inhibit the

proteolysis of hefanol. Hydrochloric acid in low concentrations ($N/920$—$N/60$) exerts no influence, but in higher concentration ($N/23$) its action is inhibitory. Other acids (phosphoric, oxalic, lactic, pyruvic, acetic, and citric acids) accelerate proteolysis up to a certain concentration, above which they exert an inhibitory action. Alkalis and sodium pyruvate have an inhibitory action. In certain cases, the nitrogen of the individual products of autolysis (peptone, ammonia, and basic nitrogen) was estimated, and the results are tabulated. S. B. S.

The Development of Alkalinity in Glomerella Cultures. HOWARD S. REED and J. THOMAS GRISSOM (*J. Biol. Chem.*, 1915, **21**, 159—163).—The fungus used was *G. rufomaculaus*, the cause of bitter rot in apples. When grown in Czapek's culture solution, which is acid, the reaction becomes alkaline in from one to two months. This is due to the formation of carbonates, ammonia, and organic bases. W. D. H.

Oxidation of Alcohol by Seedlings. W. ZALESKI (*Biochem. Zeitsch.*, 1915, **69**, 289—293).—The objects employed for the experiments were first cultivated for one or two days in solutions containing 1—2% of alcohol. They were then divided into two equal parts, in one of which the alcohol was estimated directly after drying on filter paper; the other part was placed in large flasks connected with vessels containing potassium hydroxide solution for the absorption of the carbon dioxide; after an interval, the alcohol in these plants was estimated. In all cases, both of seedlings and seeds (including those of wheat), the alcohol content was smaller than in the control portions, in which the alcohol was estimated directly after removal from the alcoholic solution. The plants appear to have the capacity of oxidising alcohol. The results are not, however, sufficient to warrant the conclusion that alcohol is a normal intermediary product of metabolism. S. B. S.

Detection and Occurrence of Nitrates and Nitrites in Plants. RICHARD KLEIN (*Biol. Zentr.*, 1915, **44**, 162—163; from *Centr. Bakt. Par.*, 1914, ii, **42**, 195).—Busch's nitron may be employed for localised precipitation of nitric acid, whilst the Griess reaction and sulphanilic acid–diphenylamine may be employed for nitrites.

Nitrites occur in the expressed sap of potato tubers, in the leaves of *Erythrina*, and in leguminous root-nodules, especially those of *Phaseolus multiflorus*. N. H. J. M.

Importance of Glycogen and Starch as Intermediate Products in the Transformations Induced by Certain Organisms. H. I. WATERMAN (*Chem. Weekblad*, 1915, **12**, 552—556).—An investigation of the percentage of invert-sugar, sucrose, and starch present in bananas dried at temperatures between 46° and 105°. A. J. W.

Glucosides Hydrolysable by Emulsin in some Papilionaceous and Scrofularinaceous Plants. Em. Bourquelot and (Mlle.) A. Fichtenholz (*J. Pharm. Chim.*, 1915, [vii], **11**, 219—226).—Out of thirteen plants examined, eleven contained glucosides which were hydrolysed by emulsin, the two exceptions being *Coronilla varia* and *Melampyrum arvense*. The largest amounts were found in the different varieties of Linaria. N. H. J. M.

Influence of Phosphorus and Magnesium on the Formation of Chlorophyll. Eva Mameli (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 755—760; this vol., i, 633). Cultures of *Zea Mais* and *Polygonum Fagopyrum* in nutrient solutions free from magnesium yield plants which are either completely etiolated or only faintly green, and contain chloroplasts of abnormal form and colour. In nutrient solutions devoid of phosphorus, the same species give plants having an intense green coloration, and containing chloroplasts of normal shape and colour. These results, which have been repeatedly confirmed, contradict those of Stoklasa (A., 1908, i, 279; 1909, i, 248), who upholds the lecithin theory of the constitution of chlorophyll, and confirm the analytical results of Willstätter and his collaborators, who find that the chlorophyll molecule contains magnesium, but not phosphorus. T. H. P.

The Rôle of Chlorophyll. P. Mazé (*Compt. rend.*, 1915, **160**, 739—742).—A series of four maize plants were cultivated in solutions, which, for the first two acting as controls, were of ordinary strength, and for the last two ten times as strong, approximately 3·4 parts of soluble elements per 1000. The amount of water evaporated by each plant was measured, and on the twentieth day this loss of water was made good by addition of the respective culture solutions, the strengths for plants 3 and 4 having reached approximately 6·2 parts per 1000. From this date, these two plants began to lag behind the controls, and six days later the terminal leaves of plant 4 were chlorotic. Comparing one control and one experimental plant, it was found that on the twenty-fourth day the control evaporated twice as much water as the other, the expenditure of heat being, therefore, 180 and 90 Cal. respectively. This difference could not be attributed to differences either in the chemical work of the plant, to external conditions, or to difference in leaf surface of evaporation. It could only come from calorific energy due to the transformation of luminous radiations by the chlorophyll. A diminution of the activity of a plant must consequently produce a decoloration of its green organs, and this was found to occur in the case of plants 3 and 4, the chlorosis being the means by which the plant protects itself against an exaggerated rise in temperature.

In the case of the control plant on the day mentioned, when the expenditure of heat due to the evaporation of the water was 180 Cal., the increase in dry weight was 2 grams. For this gain in weight, about 8 Cal. were absorbed. The author considers that the difference comes from the chlorophyll, and that it is rash

to attribute to this substance any immediate action on the chemical changes taking place during the assimilation of carbon. The rôle of the pigments of the higher plants is purely physical. W. G.

Phenomena of Oxidation and Reduction with Reference to the Chromogens of Plants. J. WOLFF and (Mlle.) NADIA ROUCHELMANN (*Compt. rend.*, 1915, **160**, 716—718. Compare A., 1914, i, 789).—The authors have examined the leaves of a large number of plants for the presence of chromogens, which under the influence of the enzyme laccase give rise to a pigment which can be reduced by hydriodic acid, iodine being liberated. The leaves were crushed with an equal weight of *N*/2-sulphuric acid, the mixture filtered, and the filtrate neutralised by the addition of a few crystals of disodium hydrogen phosphate. The liquid was then divided into two parts, one kept as a control, and to the other one or two drops of a glycerol maceration of *Russula delica*, containing the laccase, were added. To each portion was then added, successively, 0·25 c.c. of a 3% potassium iodide-starch solution and 0·15 c.c. of *N*-acetic acid. The more or less rapid appearance of a blue coloration in the second portion indicated the presence of the chromogen in the original leaf material. The plants examined are listed according to the time required for the appearance of the blue colour. Amongst those which gave negative results were oak leaves, iris leaves, acacia leaves, Brussels sprouts, carnations, and the mycelium of *Aspergillus niger*. That the results obtained were due to laccase, and not to tyrosinase, in the extract of *Russula delica* was shown by heating the extract at 70°. The oxidisable substances could not be obtained pure, but it was shown that they were easily dialysable without decomposition, and could be extracted from leaves and other plant tissues by aqueous ether if the medium was made slightly acid to prevent oxidation by any laccase present. W. G.

Phytochemical Investigation of the Fruit of Phytolacca Abyssinica. R. KUENY (*Arch. Pharm.*, 1914, **252**, 350—381).—The fruits of *Phytolacca abyssinica* (*P. dodecandra*, *Pircunia abyssinica*) were obtained from Ghinda and Asmara, in Erythraea, and botanically appeared to be identical. They were powdered, and extracted successively with light petroleum, ethyl ether, chloroform, 90% alcohol, distilled water, and cold, very dilute hydrochloric acid. The following constituents were thus obtained. *Light petroleum extract.*—(1) A *substance* (C = 77·91; H = 10·62%), colourless powder, which exhibits the reactions of a phytosterol, and appears to be an unsaturated alcohol; (2) a yellowish-brown, semi-solid, fatty mass, solidifying at 24° (acid number, 29·85; iodine value, 91·18; Reichert-Meissl number, 3·26; Polenske number, 0·7, D^{18} 0·9378), from which have been isolated the preceding substance, a *hydrocarbon* (C = 85·83; H = 14·41%), m. p. 68—69°, and a resin. *Ethereal extract.*—(3) A volatile *acid* (*calcium* salt, amorphous, yellow powder); (4) a volatile *acid*, crystals, m. p. about 56°. *Chloroform extract.*—Resinous matter. *Ninety per*

cent. alcoholic extract.—(5) A *saponin* (see below); (6) a *tannin*; and (7) a *mucilage*, which appears to yield galactose and pentoses by hydrolysis. The presence of alkaloids could not be detected. The air-dried fruit yields 7·56% of ash (K, Na, Ca, Mg, Fe, Al, P_2O_5, SiO_2, and Cl), the chief constituent being potassium ($K_2O = 23·76\%$).

The saponin is an amorphous, colourless, strongly hygroscopic substance, which exhibits the usual properties of these compounds. It is dextrorotatory in aqueous solution, forms an *acetyl* and a *benzoyl* derivative, both of which are amorphous, and is hydrolysed by boiling 3% sulphuric acid, yielding dextrose, lævulose, galactose, and a *prosapogenin*, m. p. 245—250°, colourless, amorphous powder. The physiological action of the saponin and the prosapogenin has been examined. C. S.

Amount of Oil and Amygdalin in the Kernels of Prunus domestica. Georg Kassner and Kurt Eckelmann (*Arch. Pharm.*, 1914, **252**, 402—408).—The oil obtained in 42·92% yield from the kernels by extraction with ether is a pale yellow liquid, D^{15} 0·9165, acid number 1·438, saponification number 188·1, iodine number 104, and n_D^{20} 1·4715. These values are compared with those of other observers.

The residue, after the removal of the oil, is extracted with 96% alcohol, and the solution is treated with ether. The precipitated amygdalin is purified by further treatment in the same manner, and then amounts to 1·82%.

After the removal of amygdalin, the residue was found to contain 47·18% of proteins and 5·97% of ash. C. S.

Magnesium in Albinic and Chlorotic Plants. Eva Mameli (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 262—267. Compare *Atti Ist. Bot. Pavia*, 1912, **15**, 251).—Examination of a large number of plants of different species affected with chlorosis shows that, in two cases out of every three, the chlorotic parts contain a greater proportion of magnesium than the remainder of the plants. The varying nature of the physiological causes known to provoke chlorosis probably results in the absorption of the salts being influenced in different ways. In eight cases out of nine, the proportion of magnesium is greater in the green parts of an albinic plant than in the white parts of the same individual; this result confirms the close physiological relation between chlorophyll and magnesium. The almost general constancy observed by Swart ("Die Stoffwanderung in ablebenden Blättern," 1914) in the proportion of magnesium present during the yellowing of leaves is probably due, not to errors of analysis, but to the fact that the magnesium does not migrate after scission of the chlorophyll.

T. H. P.

Chemical Investigation of Cranberry. A. Rising (*Bied. Zentr.*, 1915, **44**, 163—166; from *Kungl. Landtbr. Akad. Handl. Tidskr.*, 1914, 329—346).—The following substances were found in

cranberries: benzoic, *iso*valeric, malic, and citric acids, fermentable sugar, and a glucoside (Griebold vacciniin, $C_6H_{11}O_5Bz$). The amount of sugar varied from 5·69 to 10·39%, whilst the benzoic acid showed much greater variations (108·6—455 mg. per 100 grams), and the variations in the keeping qualities of the berries are attributed to differences in the amounts of benzoic acid. The sap of cranberries is of a light colour when expressed quickly, and becomes red when exposed to air. Cranberries can be quickly dried at 40° without loss of sugar, free acid, and benzoic acid.

N. H. J. M.

The Toxic Action of Ninhydrin. OSCAR LOEW (*Biochem. Zeitsch.*, 1915, **69**, 111—115).—The action of ninhydrin (triketohydrindine hydrate) was found to be toxic to both higher and lower organisms. The moulds formed an apparent exception, due, probably, to the impermeability of the cells. S. B. S.

The Organic Phosphoric Acid Compound in Wheat Bran. IV. Inositol Triphosphate in Wheat Bran. R. J. ANDERSON (*J. Biol. Chem.*, 1915, **20**, 463—473).—The strychnine and barium salts of a substance from wheat bran were prepared and analysed. From this, the conclusion is drawn that the organic phosphoric acid compound dealt with consisted principally of inositol triphosphate, $C_6H_{15}O_{15}P_3$. The amorphous barium salts analysed may have contained some diphosphate, and the monophosphate was isolated from the same bran. W. D. H.

The Hydrolysis of Phytin by the Enzyme Phytase Contained in Wheat Bran. R. J. ANDERSON (*J. Biol. Chem.*, 1915, **20**, 475—482).—The chief products are inorganic phosphoric acid and certain intermediate compounds consisting, probably, of inositol tri-, di-, and mono-phosphates; these are identical with the compounds previously isolated from 0·2% hydrochloric acid extracts of wheat bran. Phytose partly hydrolyses all the phytin, and completely hydrolyses some of it. W. D. H.

The Hydrolysis of the Organic Phosphorus Compound of Wheat Bran by Phytase. R. J. ANDERSON (*J. Biol. Chem.*, 1915, **20**, 483—491).—The maximum activity of the enzyme occurs in the presence of 0·1% hydrochloric and 0·2% acetic acid. With increase of acid its activity diminishes, and with 0·5% hydrochloric acid no hydrolysis occurs at all. It is destroyed by boiling with 0·5% hydrochloric acid and by 0·25% ammonia. Wheat bran normally contains about 0·1% of inorganic phosphorus, that is, about 11% of the total soluble phosphorus. W. D. H.

Phytin in Wheat Bran. R. J. ANDERSON (*J. Biol. Chem.*, 1915, **20**, 493—500).—By digesting wheat bran with 1% hydrochloric acid, phytase is destroyed, and crystalline barium salts can be isolated having the composition $C_6H_{12}O_{24}P_6Ba_3 + 8H_2O$ and $(C_6H_{11}O_{24}P_6)_2Ba_7 + 14H_2O$. These salts are identical with the tri-

barium phytate, and heptabarium phytate obtained from oats, cotton-seed meal, and commercial phytin. All these materials contain, therefore, the same organic phosphorus compound, namely, phytic acid or inositol hexaphosphate, $C_6H_{18}O_{24}P_6$. W. D. H.

Organic Phosphorus Compounds of Wheat-Bran. CHARLES J. ROBINSON and J. HOWARD MUELLER (*Biochem. Bull.*, 1915, **4**, 100—117).—A large part exists as phytin, which yields a crystalline tribarium salt. There is another substance, the barium salt of which contains only 34 instead of 38% of barium; it does not dialyse, so its molecule is probably larger. A third phosphorus compound has more carbon and less phosphorus than phytin; on hydrolysis it gives pentose, and its barium salt has only 31% of barium. It has not been obtained yet in crystalline form.

W. D. H.

Effect of Certain Organic Compounds on Wheat Plants in the Soil. FRED W. UPSON and A. R. POWELL (*J. Ind. Eng. Chem.*, 1915, **7**, 420—422).—Vanillin is not appreciably toxic to wheat plants in the soil, even when present to the extent of 1 part per 1000 parts of soil. Salicylaldehyde does not have any toxic effect when present in the soil in the proportion of 0·5 part per 1000 parts. *p*-Benzoquinone in concentrations below 0·5 part per 1000 is beneficial to the growth of wheat, whilst cumarin and dihydroxystearic acid have a slightly injurious effect. In water cultures, all these substances have a pronounced toxic effect. The effect of salicylaldehyde on the growth of wheat varies with different soils.

W. P. S.

Atmosphere of the Soil. Its Composition and the Causes of Variation. EDWARD JOHN RUSSELL and ALFRED APPLEYARD (*J. Agric. Sci.*, 1915, **7**, 1—48).—The atmosphere of the soils examined contained, on the average, 0·25 vol. % of carbon dioxide and 20·6% of oxygen, and its composition varies more than that of the atmosphere above the soil. The sum of the carbon dioxide and oxygen is usually only slightly less than that of the atmosphere; there is, however, a perceptible fall in the amount of oxygen during periods of active nitrification, and a still greater fall in water-logged soils.

The air dissolved in the soil-water and colloids consists mainly of carbon dioxide and nitrogen.

The fluctuations in the composition of the free air of the soil depend mainly on fluctuations in bacterial activity, the curves being similar to those showing the amounts of nitrate and the numbers of bacteria; the maximum values occur in the late spring and autumn, the minimum values in summer and winter. In autumn, the bacteria increase first, then the carbon dioxide, and finally the nitrates.

From November to May, the curves closely follow the soil temperature curves, whilst from May to November they follow the rainfall, and to a less extent the soil moisture, curves, the beneficial effect of the rain, apart from soil moisture, probably being due to its dissolved oxygen.

Grass land usually contains more carbon dioxide than arable land; there is, however, no evidence to show that the growing crop causes any marked increase in the amount of carbon dioxide.

N. H. J. M.

Colloidal Properties of the Acid Soils of Japan. I. and II. T. TADOKORO (*J. Coll. Agric. Tohoku Imp. Univ.*, 1914, **6**, 27—50, 117—129).—The gel forms obtained by steeping the soils in different liquids and solutions vary according to the reagent employed, indicating that in non-humus acid soils the substances which produce gels are not uniform. The differences in the increase in volume between the original soils and soils which have been extracted with water are very small in soils which contain only small amounts of humus. In such soils, the rise in temperature when steeped is probably proportional to the increase in volume, which is usually closely related to hygroscopicity. Adsorption of dyes is closely related to the increase in volume. Adsorption of ammonia has no regular relation to adsorption of dyes, to the increase in volume, or to hygroscopicity. The constant of the absorption equilibrium varies according to the concentration of the ammonium salt, and is greater in acid soils containing small amounts of humus than in soils rich in humus.

In neutral soils, the increase in volume is greatest in humus soils, less in clay soils, and least in sands; the hygroscopicity is greatest in clay soils; the adsorption of dyes and the absorption of ammonia are greatest in humus soils. In each case, sandy soils are the last.

The differences in the increase in volume with different reagents are much greater in acid than in neutral soils, due to the presence in acid soils of large amounts of colloids in unstable forms.

The adsorption of dyes is usually greater in acid mineral soils than in neutral soils. The absorption of ammonia is also generally greater in the acid soils; there is, however, no great difference between lowest absorption with acid soils and the highest with neutral soils.

N. H. J. M.

Nitrogen Compounds in Rain and Snow. FRANK T. SHUTT (*Trans. Roy. Soc. Canada*, 1914, [iii], **8**, 83—87. Compare A., 1909, ii, 429).—With an average rainfall of 862·7 mm. during the seven years ending February, 1914, the total nitrogen in the rain amounted to 6·924 kilos. per hectare per annum. This includes organic nitrogen, in addition to nitrogen as ammonia, nitrates, and nitrites. The amounts of ammonia in the rain are increased by bush fires, which occurred each year, usually in the autumn; and in 1908, when the fires were unusually extensive, the total nitrogen for the year amounted to 9·368 kilos. per hectare. High results (especially ammonia and organic nitrogen) were frequently obtained during very severe cyclonic storms, or immediately afterwards, owing to dust particles.

N. H. J. M.

Organic Chemistry.

Causes of the Formation of Petroleum. A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 714—716).—The author's results (this vol., i, 638) promise to throw light on the appearance of heterocyclic compounds of nitrogen and sulphur among products of dry distillation and also on the origin of petroleum.

Since the exact cause of the phenomenon of optical activity in organisms is unknown, the optical activity of petroleum cannot be advanced as an argument either for or against the mineral origin of petroleum. The possibility of the formation of the hydrocarbons composing the greater part of petroleum from the simplest hydrocarbons by catalytic processes is evident from Sabatier's and Ipatiev's experiments on catalysis in presence of metals and also from the author's results relating to catalytic reactions in presence of oxides and salts (*loc. cit.*). It is quite probable that the catalysts in nature belong to both of these classes, local differences in them conditioning variations in the composition of the natural products obtained.

The formation of petroleums containing as much as 4·7% of sulphur and of those containing 2·39% of nitrogen, corresponding with 20—25% of nitrogenous compounds, is explainable more readily by reactions similar to those described by the author than by animal processes. What is known of the nature of the sulphur and nitrogen compounds of petroleum also accords with their origin from such reactions. These compounds include higher pyridine and, probably, hydropyridine bases, and pyrrole; the lower bases of the pyridine series, being readily soluble in water, should be removed from the petroleum and accumulated in the water of the petroleum cavities.

T. H. P.

Fractional Composition of the Solid Paraffins in Petroleum as a Criterion for Judging its Geological Age. M. A. RAKUZIN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 641—642).—The author's conclusion, that the petroleums richest in paraffins are found in comparatively recent formations (A., 1909, ii, 490), has been repeatedly confirmed by both chemical and geological investigations. An explanation of this phenomenon is furnished by the observation that floridin, kaolin, clay, etc., extract quantitatively from petroleum the lower homologues of solid paraffins (this vol., i, 489). Assuming the occurrence of adsorption during the natural filtration-distillation of petroleum, it could be foreseen that petroleums found in the later strata should be deprived of the lower homologues of solid paraffins owing to the removal of the latter by the filtering layers of the earth. Further, the presence in the paraffins from petroleum of lower homologues indicates that such petroleum has not completed its filtration, and consequently occurs near the position of its original deposition. Grosny petroleum, for instance, is probably obtained from

comparatively deep strata, this conclusion being confirmed by its low carbonisation constant. T. H. P.

Specific Gravities of Cold and Hot Fractions of the Solid Paraffins of Petroleum. M. A. RAKUZIN and A. A. ARSENEV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 642—645).—The authors have determined pyknometrically the specific gravities of the various homologous solid paraffins obtained from Grosny petroleum (this vol., i, 489). T. H. P.

Catalytic Actions of Colloidal Metals of the Platinum Group. XIII. Hydrogenation of Ethylene with Colloidal Platinum. C. PAAL and ANTON SCHWARZ (*Ber.*, 1915, **48**, 994—1001).—The reduction of ethylene to ethane by hydrogen in the presence of colloidal palladium has already been effected (Paal and Hartmann, A., 1909, i, 545) and in the present investigation it is shown that colloidal platinum can be used in place of palladium; comparing solutions of equivalent concentration and prepared in a similar manner, palladium is somewhat more active than platinum. Curves are given showing the effect of shaking, of ageing, and of altering the concentration of the catalyst on the rate of reduction. The activity of the platinum colloid diminishes after repeated use, and although increase in the concentration of the platinum has a marked influence on the velocity of the reduction, the effect is not nearly directly proportional to the concentrations employed. D. F. T.

Syntheses with the Aid of Acetylene. A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 703—713).—Study of the reactions undergone by acetylene when heated in presence of different catalysts shows that they consist of three principal processes: (1) Local decomposition of the acetylene into carbon and hydrogen, accompanied by polymerisation into aromatic hydrocarbons; (2) condensation to solid hydrocarbons, similar to cuprene; (3) hydrogenation of acetylene and aromatic hydrocarbons with formation of hydrocarbons of the paraffin, olefine, and cyclic series. In general, these reactions do not proceed smoothly, and, according to Sabatier, are accompanied by resolution of the hydrocarbon molecules into the residues, CH_3, CH_2, and CH, which then undergo combination in various ways. From the results of Ipatiev's experiments on the condensation of ethylene in presence of alumina and at a high pressure, it might be expected that the condensation of the more highly unsaturated acetylene would take place comparatively readily even at ordinary pressure. This is actually found to be the case.

Acetylene and ammonia, when passed over alumina, ferric oxide, or chromic oxide heated at slightly above 300°, react, giving principally pyridine bases. These consist mainly of α- and γ-picolines in almost equal proportions, together with 2-methyl-3-ethylpyridine. Pyrrole, secondary piperidine bases, neutral compounds, and hydrogen are also formed. The three principal types of condensation are, therefore, as follows: $2C_2H_2 + NH_3 = C_4H_5N + H_2$, $3C_2H_2 + NH_3 = C_6H_7N + H_2$, and $4C_2H_2 + NH_3 = C_8H_{11}N$. The quantitative composition of the con-

densate obtained varies with the catalyst, the proportion of pyrrole being increased by replacing alumina by ferric oxide. Similar mixtures are obtained when the catalyst consists of an oxide of a quadrivalent element, such as titanium, thorium, or silicon, or of various salts of tervalent metals, such as aluminium phosphate, kaolin, etc., but the latter require somewhat higher temperatures. Ethylene also yields pyridine bases under the above conditions, but here, also, higher temperatures are necessary, and it is probable that the reactions are preceded by decomposition of the ethylene, with formation of acetylene.

When passed over heated alumina, a mixture of acetylene with either hydrogen sulphide or sulphur vapour condenses to form thiophen at comparatively low temperatures, but the reaction proceeds rapidly only at temperatures rather higher than those employed by Steinkopf and Kirchoff (A., 1914, i, 425) for the action of acetylene on pyrites. The thiophen is accompanied by small proportions of higher homologues, such as ethylthiophen. This method is even more satisfactory than that of Steinkopf and Kirchoff for the preparation of thiophen on a large scale, since it yields a purer product and is not accompanied by appreciable charring of the acetylene. Furan may be similarly obtained by passing acetylene and water vapour over alumina heated at 400—425°.

Dry acetylene, in presence of alumina at 400°, gives a mixture of unsaturated and aromatic hydrocarbons, benzene constituting less than 10% of the liquid product; the various compounds formed are being investigated.

The condensation of acetylene with ammonia by heated alumina sometimes yields acetaldehyde-ammonia, and the conclusion is drawn that the first phase of the reaction consists of the combination of acetylene and water with formation of acetaldehyde, which then takes part in the condensation, the water thus liberated uniting again with acetylene, and so on. Thus, the traces of water which cannot be excluded play the part of a catalyst. This conclusion is in agreement with the observation that acetaldehyde-ammonia is the principal product obtained when moist acetylene and ammonia are passed through a heated tube charged with oxides of the heavy metals of the type RO, such as ferrous, zinc, or nickel oxide; under the same conditions, moist acetylene alone gives a liquid product containing, besides compounds of high boiling point, acetaldehyde and crotonaldehyde. It is found, further, that when ammonia and an aldehyde are passed together over alumina heated at above 300°, they yield all those pyridine bases which have been obtained from the reagents under other conditions (compare A., 1906, i, 451), and exhibit also a new type of condensation resulting in the formation of homologues of pyridine with the side-chain in the 4-position; thus, ammonia, acetaldehyde, and benzaldehyde give 2- and 4-phenylpyridines. Doebner and Miller's reaction between acetaldehyde and aniline yields 2-methylquinoline, and the author finds that acetylene and aniline vapour, when passed over alumina at 360—420°, give, together with other products, indole and homologues of quinoline, 4-methylquinoline and not 2-methylquinoline being formed in predominating proportion. Careful investi-

gation of the products of Doebner and Miller's reaction shows that these contain, in addition to 2-methylquinoline, also a small proportion of 4-methylquinoline. T. H. P.

Catalytic Reduction of Organic Halogen Compounds. W. BORSCHE and G. HEIMBÜRGER (*Ber.*, 1915, **48**, 850. Compare this vol., i, 527).—The authors have ascertained that the reduction of organic halogen compounds by catalytic means has been carried out in Wallach's laboratory during recent years, and has even been recommended for the purposes of estimating halogens (Busch, *Zeitsch. angew. Chem.*, 1914, **27**, 432). J. C. W.

Use of Iodine as a Dehydrating and Condensing Agent. HAROLD HIBBERT (*J. Amer. Chem. Soc.*, 1915, **37**, 1748—1763).—It was observed by the author that the disadvantages connected with the use of most of the usual condensing agents could be avoided and satisfactory yields of unsaturated derivatives obtained by heating the hydroxy-compound with a minute quantity of iodine. When *iso*hexan-δ-ol-β-one (diacetone alcohol) is heated alone under ordinary pressure, it boils at about 164° and decomposes considerably with formation of acetone. On distillation in presence of a minute quantity of iodine, however, it decomposes almost quantitatively into water and mesityl oxide. The use of iodine in this way as a dehydrating and condensing agent has now been found capable of general application.

An account is given of experiments in which iodine was employed for the conversion of alcohols into unsaturated hydrocarbons, of ketonic alcohols into unsaturated ketones, of aldols into unsaturated aldehydes, and of glycols and glycerols into polyglycols and polyglycerols, and for the condensation of aldehydes with polyhydric alcohols.

A theory is proposed to explain the catalytic action of the iodine in such processes. E. G.

Union of Hydrogen with Acetylenic Derivatives. V. Hydrogenation of Tetraethylbutinenediol [γζ-Diethyl-Δ$^{\delta}$-octinene-γζ-diol]. Y. S. ZALKIND and N. K. BYSTRJAKOV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 680—688).—γζ-Diethyl-Δ$^{\delta}$-octinene-γζ-diol has m. p. 77—78·5°, b. p. 110—115°/13 mm.; Iocitsch (A., 1914, i, 375) gave m. p. 73°, b. p. 140—141°/20 mm. This compound was hydrogenated in the manner previously described (compare Zalkind, A., 1914, ii, 257, 258), the results showing that it belongs to the class of glycols which combine with difficulty with hydrogen. Even when a greater proportion of catalyst is employed than with βε-dimethyl-Δ$^{\gamma}$-hexinene-βε-diol, the reaction proceeds slowly, especially towards the end.

When platinum black is used as catalyst, the combination with hydrogen at 18—19° is rapid, and the value of k, calculated for a uni-molecular reaction, correspondingly high until 50% of the total hydrogen has been combined. The reaction then gradually slackens as far as 90% of hydrogen, after which the value of k begins to increase, in consequence of reduction to the saturated alcohol. The latter reaction proceeds slowly, its influence being appreciable only

when the original hydrogenation approaches completion. The velocity constant diminishes only slightly more slowly than the proportion of catalyst taken, values of k related as 4·25 : 1·63 : 1 being obtained with amounts of platinum in the ratios 5 : 1·67 : 1.

When colloidal palladium is used instead of platinum, the acetylenic glycol exhibits still greater difficulty in combining with hydrogen. The values obtained when 0·01, 0·02, and 0·03 gram of the catalyst are employed per 1·98 gram (0·01 gram-mol.) of the glycol remain constant until 90% of the theoretical amount of hydrogen enters into combination and, further, are approximately equal, namely, 0·041, 0·040, and 0·044. Use of 0·005 gram instead of 0·01 gram of the catalyst results in marked diminution in the initial velocity, which then begins to diminish after combination of 50% of the hydrogen. The failure of the proportion of catalyst to influence the velocity of the reaction in the above three instances is probably due to the fact that γζ-diethyl-Δ$^{\delta}$-octinene-γζ-diol exerts a greater retarding effect than βε-dimethyl-Δ$^{\gamma}$-hexinene-βε-diol. Similar independence of the velocity of the reaction on the proportion of catalyst has been observed in certain fermentative processes, for instance in the action of emulsin on salicin (compare Tammann, A., 1896, ii, 244) and in that of large proportions of pepsin (compare Woker, "Die Katalyse," Stuttgart, 1910, 152).

γζ-Diethyloctane-γζ-diol, $C_2H_4(CEt_2{\cdot}OH)_2$, forms odourless crystals, m. p. 66—67·5°, has the normal molecular weight in boiling ether, and forms a liquid acetyl derivative with a pleasant odour. When heated with dilute sulphuric acid, it yields the corresponding *oxide*, $C_{12}H_{24}O$, which is a colourless liquid, b. p. 204—206° or 89—90°/9 mm., with a pleasant odour.

γζ-Diethyl-Δ$^{\delta}$-octene-γζ-diol, $C_2H_2(CEt_2{\cdot}OH)_2$, forms odourless, acicular crystals, m. p. 77—78·5°, exhibits normal ebullioscopic behaviour in ether, and decolorises solutions of bromine and of alkaline permanganate. It gives no marked coloration with concentrated sulphuric acid, whereas γζ-diethyl-Δ$^{\delta}$-octinene-γζ-diol gives an intense orange-yellow colour. T. H. P.

Union of Hydrogen with Acetylenic Derivatives. IV. Hydrogenation of Diphenyldimethylbutinenediol [βε-Diphenyl-Δ$^{\gamma}$-hexinene-βε-diol. Y. S. Zalkind and K. V. Kvapischevski (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 688—703).—The authors have investigated the hydrogenation of the two isomeric βε-diphenyl-Δ$^{\gamma}$-hexinene-βε-diols (compare Iocitsch, A., 1914, i, 375; Dupont, A., 1910, i, 379) in alcoholic solution in presence of colloidal palladium and in ethereal solution in presence of platinum black (compare A., 1914, ii, 257, 258).

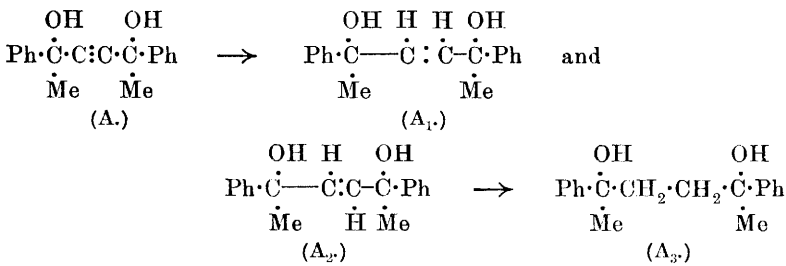
In the former case, the hydrogenation at 15° follows different courses with the two isomerides. Isomeride I, m. p. 163°, combines with two atoms of hydrogen in six hours, and isomeride II, m. p. 125—127°, in 100 minutes, 80% undergoing hydrogenation to the corresponding ethylenic glycol in 140 and 30 minutes respectively; the mean values for k are 0·0090 and 0·0260. With the second isomeride, k remains moderately constant throughout, whilst with the first, it

shows a continuous fall, excepting towards the end of the absorption, when a slight rise occurs. If the proportion of colloidal palladium used with isomeride I is doubled, k exhibits a similar degree of constancy to that found with isomeride II (compare Zalkind and Pischtschikov (this vol., ii, 435). The velocity of hydrogenation varies with the properties of the colloidal palladium employed. Further, the values of k, at least during the initial stages of the hydrogenation, are very nearly proportional to the relative amounts of palladium present.

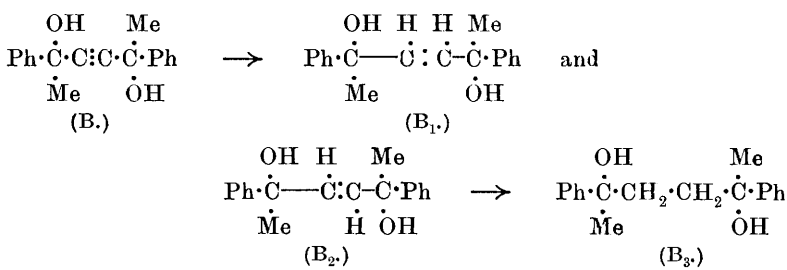
When the complete hydrogenation of these acetylenic glycols to saturated glycols in presence of platinum black is studied, it is found that the two isomerides again exhibit marked differences in behaviour, but in this case compound I reacts with far greater velocity than compound II, double the proportion of catalyst being required with the latter in order to give the same value of k as with isomeride I.

In general the hydrogenation of these compounds in presence of platinum black exhibits retardation after two atoms of hydrogen have been combined, but such retardation is comparatively slight. When, however, colloidal palladium is used, hydrogenation proceeds comparatively rapidly until the amount of hydrogen absorbed corresponds with the formation of the ethylenic glycol and subsequently takes place only very slowly, the curve exhibiting a sharply defined change of direction. These results are in accord with those obtained with other acetylene derivatives (*loc. cit.*).

Each of the two isomeric $\beta\epsilon$-diphenyl-Δ^{γ}-hexinene-$\beta\epsilon$-diols should be capable of yielding two ethylene and one saturated glycols. Thus, for the syn-compound:



A similar scheme holds good for the anti- or racemic-compound:



$\beta\epsilon$-Diphenyl-Δ^{γ}-hexinene-$\beta\epsilon$-diol I (m. p. 163°) gives *$\beta\epsilon$-diphenyl-Δ^{γ}-hexene-$\beta\epsilon$-diol* I, $C_2H_2(CPhMe\cdot OH)_2$, m. p. 97—102°, which has the

normal molecular weight in boiling acetone, gives a faint yellow coloration with concentrated sulphuric acid, decolorises alkaline permanganate solution, and combines with bromine. Treatment of the glycol with bromine in chloroform solution results in the evolution of hydrogen bromide and the formation of a single *bromo*-derivative, $C_{18}H_{19}O_2Br$, which forms crystals, m. p. 161°. Since this ethylene glycol is not converted into the corresponding oxide when treated with dilute sulphuric acid, it is assumed to be an anti-compound of structure A_2 or B_2.

$\beta\epsilon$-Diphenyl-Δ^γ-hexinene-$\beta\epsilon$-diol II (m. p. 125—127°) gives *$\beta\epsilon$-diphenyl-Δ^γ-hexene-$\beta\epsilon$-diol* II, $C_2H_2(CPhMe\cdot OH)_2$, m. p. 110°, which shows normal ebullioscopic behaviour in acetone, and towards concentrated sulphuric acid and alkaline permanganate behaves in the same way as its isomeride. When boiled with dilute sulphuric acid it gives, however, the corresponding *oxide*, $C_{18}H_{18}O$, which is a liquid with a faint, pleasant odour, and has the normal molecular weight in boiling acetone. The hexenediol II is, therefore, regarded as a syn-compound of structure A_1 or B_1.

$\beta\epsilon$-Diphenylhexane-$\beta\epsilon$-diol I, $C_2H_4(CPhMe\cdot OH)_2$, corresponding with the hexenediol I, forms odourless, white crystals, m. p. 142°, has the normal molecular weight in boiling acetone, and gives a faint, yellow coloration with concentrated sulphuric acid.

$\beta\epsilon$-Diphenylhexane-$\beta\epsilon$-diol II, $C_{18}H_{22}O_2$, corresponding with the hexenediol II, forms small, crystalline columns, m. p. 154°, gives the normal molecular weight in boiling acetone, and is converted by hot dilute sulphuric acid into the corresponding *oxide*, $C_{18}H_{20}O$, which forms white crystals, m. p. 72°.

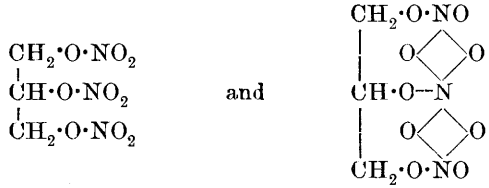
Consequently, acetylenic glycol, m. p. 163°, → ethylenic glycol (anti-form), m. p. 97—102° → saturated glycol, m. p. 142°, and acetylenic glycol, m. p. 125—127°, → ethylenic glycol (syn-form), m. p. 110°, → saturated glycol, m. p. 154°. It has not yet been established which of these series corresponds with configuration A and which with configuration B. T. H. P.

Constituents of Animal Fats. The Fat of Caballus Equus. J. KLIMONT, E. MEISL and K. MEYER (*Monatsh.*, 1914, **35**, 1115—1127). —By repeated crystallisation of the fat, derived from various parts of the horse, from a mixture of acetone and chloroform, and finally from ether, the authors have isolated a glyceride, m. p. 60°, saponification number 856·4, which, on hydrolysis, yields heptadecoic (margaric) acid, and therefore consists of triheptadecoin (trimargarin). The liquid portion of the fat contains glycerides of oleic, linolic, and linolenic acids. For full details of the detection and separation of the above substances the original must be consulted.

In view of the occurrence of heptadecoic acid in horse fat and also in oil of coffee beans (Meyer and Eckert, A., 1911, i, 106), the authors are of the opinion that this acid is more widely distributed in fats than has hitherto been imagined, and that many of the supposed eutectic mixtures of palmitic and stearic acids really consist of heptadecoic acid. This, for example, has been shown to be the case with the

eutectic mixture isolated by Klimont and Meisl (A., 1909, ii, 597) from goose fat. F. B.

Nitroglycerin [Glyceryl Trinitrate.] III. Nature of the Isomerism of Nitroglycerin and Sensitiveness of the Frozen Product to Shock. HAROLD HIBBERT (*Chem. Zentr.*, 1914, ii, 1097—1098; from *Zeitsch. ges. Schiess. Sprengstoffwesen*, 1914, **9**, 305—307, 321—322).—The author compares the phenomena observed with the previously described isomerides of glyceryl trinitrate with other transformations recorded in the chemical literature and is led to the conclusion that the solid labile and stable compounds are chemically isomeric—possibly in the sense of the formulæ:



Each isomeride can retain its structure in the liquid state; freshly prepared glyceryl trinitrate is generally a mixture of a large amount of the liquid labile isomeride and a small quantity of the liquid stable isomeride.

A number of theories are advanced in explanation of previously recorded observations, and, particularly, of the sensitiveness of the frozen product to shock. H. W.

Complex Compounds of Platinum with Organic Tellurides. E. FRITZMANN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 588—590. Compare A., 1912, i, 71).—*Benzyl telluride platinous chloride*, $PtCl_2,2(CH_2Ph)_2Te$, prepared by mixing an alcoholic solution of benzyl telluride (compare Tschugaev and Chlopin, A., 1914, ii, 455) with aqueous potassium platinochloride, or by the interaction of benzyl telluride and tripropylamine platinochloride (compare Tschugaev, A., 1914, i, 1054) in absolute alcohol, forms an orange powder, and in solution, especially when heated, readily undergoes decomposition into tellurium, platinum and dibenzyl; it may, however, be separated rapidly from its chloroform solution as a microcrystalline, greenish-orange powder. In the solid state it remains unchanged for months. It begins to decompose at 115—120°, and is not melted even at 200°. In freezing bromoform it exhibits the normal molecular weight. The method of formation of the compound and its properties indicate that it has the co-ordination formula, $[Pt\{(CH_2Ph)_2Te\}_2Cl_2]$.

The estimation of the platinum and tellurium in the compound was carried out as follows. A weighed quantity was evaporated at least twice nearly to dryness with 50 c.c. of aqua regia, the residue was dissolved completely in hot water and the solution, after acidification with hydrochloric acid, heated to boiling and precipitated with a hot saturated solution of hydrazine sulphate, the liquid being then kept gently boiling for about thirty minutes. The black precipitate was then introduced on to a weighed filter, washed with boiling water, dried at

110° for not longer than an hour, and weighed. This weight represents the platinum and tellurium together. The tellurium was removed by evaporation with fuming nitric acid and the residual platinum heated to constant weight. T. H. P.

Preparation of Ammonia and Formic Acid. H. Haakh (D.R.-P. 281044; from *J. Soc. Chem. Ind.*, 1915, **34**, 611).—Ammonia and formic acid are formed when compounds like the ferrocyanides are heated with water or bases. The reaction in the case of potassium ferrocyanide is given by the equation:

$$K_4Fe(CN)_6 + 14H_2O = 4H\cdot CO_2K + 2H\cdot CO_2NH_4 + 4NH_3 + Fe(OH)_2.$$

If the decomposition is brought about by potassium hydroxide solution, the filtrate from the ferrous hydroxide, after boiling off the ammonia, is a pure solution of potassium formate. J. C. W.

Vapours from Drying Paint Films. H. H. King (*J. Ind. Eng. Chem.*, 1915, **7**, 502—504. Compare A., 1914, i, 380; this vol., i, 117).—Experiments carried out by the author afforded evidence that carbon monoxide is one of the gaseous products given off in the drying of paint films; the production of the gas does not appear to be favoured by the presence of any one pigment. Klein (*loc. cit.*) has pointed out the well established fact that linseed oil films give off formic acid during drying, and, since fuming sulphuric acid decomposes this acid with the formation of carbon monoxide, the passage of the gaseous products from drying paint through sulphuric acid previous to the application of tests for carbon dioxide is inadvisable. In the author's experiments, the gaseous products were passed through barium hydroxide solution before the carbon monoxide was estimated by the iodine pentoxide method. The quantity of carbon monoxide found was extremely small, and no serious danger would be likely to arise in dwellings, as the gas would be too highly diffused, and removed to cause any harm. W. P. S.

Preparation of Acetic Acid from Acetylene. Chemische Fabrik Griesheim-Elektron (Fr. Pat. 473158; from *J. Soc. Chem. Ind.*, 1915, **34**, 491).—Acetylene, oxygen, and the requisite amount of water are caused to react in the presence of mercury compounds, such as the acetate, sulphate or phosphate, and in acetic acid, or any organic acid like chloroacetic or lactic acid which can easily be separated from the acetic acid formed. Contact substances such as iron oxides or vanadium pentoxide, and accelerating agents like phosphoric acid, sulphuric acid or hydrogen sulphates are recommended. The gases should be introduced alternately, in small quantities, into the acid mixture. Ethylidene diacetate is formed intermediately if glacial acetic acid is the medium. J. C. W.

The Comparative Volatility by Distillation with Steam of Some Organic Acids. W. Œchsner de Coninck and R. Raynaud (*Rev. gen. Chim. pure appl.*, 1914, **17**, 201—202).—A comparison of the volatility of formic, acetic, propionic, butyric, and *iso*butyric acids when distilled with an excess of water. In each case 5 c.c. of the

acid were mixed with 25 c.c. of water and distilled, the distillate being collected in 5 c.c. portions and the amount of acid in each portion estimated. With formic and acetic acids the amount of acid present in each fraction steadily increases as the distillation proceeds; with propionic acid it remains constant, and with butyric and *iso*-butyric acids decreases. W. G.

Trichloroacrylic Acid and Some of its Derivatives. II. J. Böeseken and J. F. Carrière (*Rec. trav. chim.*, 1915, **34**, 179—186. Compare A., 1913, i, 821).—Attempts to purify trichloroacrylic acid by distillation under reduced pressure (30 mm.) resulted in a portion of the acid being converted into its anhydride. The acid shows marked association when dissolved either in benzene or in nitrobenzene, whilst in water it is almost completely dissociated. The authors have studied the system, water–trichloroacrylic acid, by determining the solidification points of mixtures containing slowly increasing percentages of the acid. The results are set out in detail, and two curves given in the original. W. G.

Composition, Structure, and Properties of Gynocardinic Acid and some of its Derivatives. I. I. Ostromisslenski and A. M. Bergman (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 318—334).—Crude gynocardinic acid consists of a mixture of isomeric, unsaturated acids, $C_{17}H_{33}\cdot CO_2H$. The pure acid, separated either by fractional crystallisation from alcohol or by means of the copper salt, forms small leaflets or plates resembling naphthalene crystals, m. p. 67·5—68·5°, and only with difficulty yields accurate results on combustion. Its salts with the alkali metals form typical soaps; the barium salt was also prepared. The copper salt (*Cuprum gynocardicum*) exists in two modifications: *α-Copper gynocardinate* forms a dark green or bluish green, amorphous mass, m. p. 69·5—70·5°, plastic at the ordinary temperature, and soluble in ether and other solvents and in fats. It forms double salts with copper acetate,

$$(C_2H_3O_2Cu)_m,[(C_{17}H_{33}\cdot CO_2)_2Cu]_n,$$

and with barium, calcium and zinc chlorides, all of these being insoluble in solvents of the original salt. When heated for a short time in solution, it assumes a cinnamon-brown colour, the original tint slowly returning when the solution is kept in a closed vessel. On prolonged heating or on storing in a hermetically sealed vessel, the α-copper salt is converted into the polymeric, insoluble β-form, which melts at a considerably higher temperature. The acid, separated from the β-salt and again treated with cupric acetate, yields only the α-salt.

Methyl gynocardinate, $C_{17}H_{33}\cdot CO_2Me$, forms a buttery liquid with a pleasant odour and blue fluorescence, b. p. 320—330°.

Treatment of the solid acid with concentrated sulphuric acid converts it into hydroxygynocardinic acid, which forms sphero-crystals of prismatic needles and has an odour recalling that of stearic acid. Gynocardinic acid gives a yellow coloration with tetranitromethane, decolorises alkaline permanganate, and unites with hydrogen haloids and bromine. The *dibromide*, $C_{17}H_{33}Br_2\cdot CO_2H$, forms an almost

colourless, buttery liquid, solidifying to a snow-white, crystalline mass at 0°, and crystallising in prismatic needles from acetone at 0°.

T. H. P.

Free and Combined Organic Acids in Worts and Beer. W. WINDISCH and K. TEN DOORNKAAT KOOLMAN (*Chem. Zentr.*, 1914, ii, 796; from *Woch. Brau.*, **31**, 225—229, 235—237, 252—255, 275—282, 295—296, 303—308, 311—316).—The greater the amount of basic substances in worts, resulting from large amounts of calcium carbonate in the mash water, the greater is the tendency of the yeast to produce organic acids. As regards lactic acid the amount depends on a variety of causes, mainly the mash process and the amount of alkali in the medium.

The increase in acidity is best estimated by titration with sodium hydroxide in presence of litmus, whilst with methyl-orange the amount of bases combined with organic acids may be estimated.

The acidity of beer depends on the malt employed, on the amount of salts present in the water, on the mash process, on the race of yeast, and on the treatment of the unfinished product. The volatile acids are mostly free and the fixed acids mostly combined; whilst lactic acid holds an intermediate position, one-third being free and the rest combined.

N. H. J. M.

Reactions of Ethyl Sodiomalonate. I. C. LORING JACKSON and F. C. WHITMORE (*J. Amer. Chem. Soc.*, 1915, **37**, 1522—1537).—The work of Jackson and Robinson (A., 1890, 377) and of Jackson and Bigelow (A., 1912, i, 101) has led to the following explanation of the reactions of ethyl sodiomalonate. When a halogenated organic substance reacts with ethyl sodiomalonate, an additive compound is first produced by the attachment of the halogen and the organic radicle to the enolic form of the ester, thus:

$$OEt\cdot C(ONa):CH\cdot CO_2Et + RX = OEt\cdot CX(ONa)\cdot CHR\cdot CO_2Et.$$

Owing to the attraction of the sodium, the negative part of the compound is added to the carbon atom bearing the ONa group. In most cases, this would be the halogen atom, X, and the compound would readily undergo the following decomposition:

$$OEt\cdot CX(ONa)\cdot CHR\cdot CO_2Et = NaX + CO_2Et\cdot CHR\cdot CO_2Et.$$

In some cases, however, the organic radicle is more negative than the halogen, especially if the latter is iodine, and the additive compound then has the formula $OEt\cdot CR(ONa)\cdot CHX\cdot CO_2Et$, and will break up into $RNa + CO_2Et\cdot CHX\cdot CO_2Et$ unless the radicle cannot combine with sodium. In the last case, the additive compound should be much more stable than in the two preceding cases, but, on acidification, the hydrogen compound of the radicle, RH, would be formed together with the halogenated ester, $CO_2Et\cdot CHX\cdot CO_2Et$.

The reaction between ethyl sodiomalonate and 1-bromo-2 : 4 : 6-triiodo-3 : 5-dinitrobenzene (Jackson and Bigelow, *loc. cit.*) has been submitted to further study, and an additive *compound*,

$$C_6BrI_3(NO_2)_2,OEt\cdot C(ONa):CH\cdot CO_2Et,$$

has been isolated. This substance is usually obtained as a dark red, amorphous solid, but on one occasion it appeared in the form of

clusters of needles. It is quite stable when not exposed to the air, but is decomposed by water or dilute acid. The decomposition with acid results in the formation of 1-bromo-2 : 6-di-iodo-3 : 5-dinitrobenzene and ethyl iodomalonate; if, however, an excess of ethyl sodiomalonate is present, ethyl ethanetetracarboxylate is produced.

An improved method is described for the preparation of 2 : 4 : 6-tri-iodoaniline. *Di-iodoaniline hydrochloride* darkens at 185° and melts at 207° (decomp.). E. G.

Ethyl Succinylsuccinate. Study of its Constitution, Some Derivatives, and Absorption Spectra. H. D. GIBBS and H. C. BRILL (*Philippine J. Sci.*, 1915, **10**, [*A*], 51—61).—When the mother liquor, from which ethyl succinylsuccinate has been obtained, is concentrated, a small quantity of a yellow, crystalline substance separates which differs considerably in its properties from the first product. The primary product has a very slight greenish-yellow colour, m. p. 127°, is less soluble in alcohol, absorbs bromine readily, and shows an absorption band at $1/\lambda = 2660$. The yellow substance melts at 123°, is more soluble in alcohol, does not absorb bromine, and the absorption band at $1/\lambda = 2660$ is more persistent than that of the former. According to Meyer's method of estimating the enol form, the pale yellow substance consists of about 90% of enol, whilst the other is found to represent the pure keto form. These observations show that ethyl succinylsuccinate exists in the form of enolic and ketonic modifications. It is probable that the pure enol form is colourless, whilst the yellow colour of the keto-form is due either to general absorption or to the extension of an absorption band which borders on the visible region.

The effect of alkali on the absorption spectra of the two isomerides has been examined, and photographs of the spectra of the diacetyl derivative and of the di-imide were obtained, which were compared with the spectra of methyl salicylate and of methyl *o*-acetoxybenzoate. The relations exhibited by the absorption curves afford evidence of a close similarity between methyl salicylate and the enol form of ethyl succinylsuccinate. The fixation of the labile hydrogen atom or the saturation of the free affinities of the oxygen atoms in the para-position destroys the absorption band. H. M. D.

The Formation of Humic Substances from Organic Substances. WILLIAM BEECROFT BOTTOMLEY (*Biochem. J.*, 1915, **9**, 260—268).—On boiling sugars with hydrochloric acid, a mixture of humic acid and humin substances is obtained, varying in proportion with the sugar used; the composition of the humic acid approximates very closely to that of the natural acid from soil or peat.

Humic acid and humin are also produced from sugars by lactic, acetic, and other organic acids, or by heat alone. These substances are not obtainable from proteins free from carbohydrates. W. D. H.

Aldehyde-ammonia and Chloral-ammonia. OSSIAN ASCHAN [with Y. VASKIO] (*Ber.*, 1915, **48**, 874—891).—According to Delépine

(1897–1899) aldehyde-ammonia is a trihydrate of a trimethylhexahydrotriazine, $CHMe<^{NH\cdot CHMe}_{NH\cdot CHMe}>NH$. If this is so, it should form two geometric isomerides. The present work was undertaken with the idea of preparing the unknown isomeride, but this was not accomplished. Some light on the chemistry of aldehyde-ammonia is afforded, however, by other observations.

In the first place, it is found that aldehyde-ammonia can be crystallised from hot water. It may be prepared conveniently by mixing concentrated aqueous ammonia and acetaldehyde at below 0°, shaking the mixture with a little ether for an hour or so, and then leaving for a day in the cold. Both the white crystals which separate (yield 56%) and the product obtained by crystallisation from hot water have m. p. 95—99°, which is much higher than the recorded m. p., 70—80°. In all the usual organic solvents the substance loses ammonia on boiling, so ebullioscopic measurements of the molecular weight were made in acetaldehyde. The constant for this solvent was obtained by means of *l*-borneol and benzophenone and found to be 11·8. Even in acetaldehyde, the aldehyde-ammonia was found to undergo dissociation, for the observed molecular weight was about half that required by the formula C_2H_7ON. Cryoscopic measurements in water gave values which approximated to the formula $(C_2H_7ON)_3$ at first, but after leaving the solutions for twenty hours or so, the values agreed with $(C_2H_7ON)_2$. If the trimeride is a trihydrate of the above triazine ring, it should compare in stability with cyanuric acid, but the facts that the trimeride breaks down into a dimeride, and is so easily decomposed by dilute acids or boiling organic solvents, are contrary to the assumption of a stable ring structure. The use of aldehyde-ammonia in such cases as the synthesis of alanine (which can be carried out with the aqueous aldehyde-ammonia) and the pyridine synthesis, argues for the view that the C_2H_7ON residues are linked by the nitrogen atoms.

The author's theory is, therefore, that the unknown unimolecular aldehyde-ammonia (which would probably be a liquid) exists in old solutions as the compound (I), and in the solid state as the trimeride (II), thus:

$$2OH\cdot CHMe\cdot NH_2 \longrightarrow \underset{(I.)}{OH\cdot NH_2(CHMe\cdot OH)(CHMe\cdot NH_2)} +$$

$$OH\cdot CHMe\cdot NH_2 = \underset{(II.)}{OH\cdot CHMe\cdot NH_2(OH)\cdot CHMe\cdot NH_2(OH)\cdot CHMe\cdot NH_2}$$

Delépine also described an anhydrous aldehyde-ammonia, which can be obtained in glistening cubes, m. p. 85°, by leaving the hydrate over sulphuric acid in a vacuum desiccator. It is now shown that the ordinary aldehyde-ammonia is immediately precipitated when water is added to the solution in chloroform. Ebullioscopic determinations of the molecular weight show that the substance suffers dissociation even in ether or acetaldehyde. The values obtained in cold benzene agree with those of Delépine, but are interpreted in favour of the formula $CHMe{:}N\cdot CHMe\cdot NH\cdot CHMe\cdot NH_2$. If this compound lost ammonia, it should form an analogue, $CHMe(N{:}CHMe)_2$, of hydrobenzamide,

$CHPh(N:CHPh)_2$. This might well be brought about, and then a difference between aromatic and aliphatic aldehydes would disappear.

When aldehyde-ammonia is prepared by passing ammonia into an ethereal solution, the filtrate contains a very soluble by-product, $C_6H_{18}O_3N_2$. As much as a 20% yield may be isolated by quickly evaporating the solvent by a blast of dry air, dissolving the residue again in the same volume of ether, filtering, and evaporating as before. The new compound forms glistening, white leaflets, m. p. 45—47°, decomp. 70—80°, but decomposes in a few hours. The molecular weight in cold benzene was found to agree with the above formula, and in view of the instability of the substance, it is regarded as *dihydroxytriethylidenedi-imine* (III), formed by the condensation of acetaldehyde with the dimeride (I), thus:—

$$OH\cdot CHMe\cdot NH\cdot CHMe\cdot NH_2 + CH_3\cdot CHO = CHMe(NH\cdot CHMe\cdot OH)_2$$
(III.)

The above new observations on acetaldehyde led to a study of chloral-ammonia. A pure preparation was obtained by passing ammonia into a chloroform solution of chloral (Schiff, 1877) or into a cold solution of dry chloral hydrate in ether. The compound forms small, granular crystals, m. p. 72—74°, which dissociate in aqueous solution. The values for the molecular weight observed in cold benzene agreed, as did those of Delépine, with the formula $C_4H_8O_2N_2Cl_6$. When left over calcium chloride in a vacuum desiccator for a few days, it lost ammonia and gave a compound, m. p. 51—53°, the molecular weight of which in cold benzene corresponded with $C_4H_5O_2NCl_6$. The substance recombined with ammonia in benzene solution. These compounds are regarded as the *hydrate* of *hydroxy-aminobistrichloroethylidene-imine*,

$$OH\cdot CH(CCl_3)\cdot NH\cdot CH(NH_2)\cdot CCl_3,H_2O,$$

which is the analogue of the dimeride (I), and *dihydroxybistrichloro-ethylidene-imine*, $NH[CH(OH)\cdot CCl_3]_2$. The latter compound is the aliphatic analogue of "benzaldehyde-ammonia," $NH(CHPh\cdot OH)_2$ (Francis, A., 1909, i, 588), and therefore brings the aliphatic and aromatic aldehydes into line, even in respect to their compounds with ammonia. J. C. W.

Pentosuria. Ernst Zerner and Rudolfine Waltuch (*Monatsh.*, 1914, **35**, 1025—1036).—When mixed with *l*-xylosephenylosazone, the m. p. of the phenylosazone of urinary pentose is elevated to 199—201°. The pentose must therefore be *l*-lyxose, *d*-xylose or the xyloketose corresponding with these aldoses (compare A., 1914, i, 230; Levene and Forge, A., 1914, i, 1027).

Polarimetric examination of the urine after removal of the nitrogenous substances shows that the pentose is dextro-rotatory, and thus cannot be identical with *d*-xylose which is lævorotatory.

It forms with dimethylhydrazinodiphenylmethane (Braun, A., 1908, i, 700, 737) an *osazone* approximating in composition to the formula $C_{40}H_{48}O_6N_8$, but whether this osazone is derived from *l*-lyxose or xyloketose could not be determined.

Dimethylhydrazinodiphenylmethane forms with glycuronolactone a *dihydrazone*, $C_{27}H_{32}O_{10}N_4$, slender, white needles, m. p. 164° (decomp.); with *d*-lyxose it forms a dihydrazone, m. p. 156°, and not 171° as given by Braun.

Braun's statement that his dihydrazine does not react with ketoses is incorrect, for *d*-fructose yields an amorphous, brown *osazone*, $C_{42}H_{52}O_8N_8$, which is not completely fused at 200°.

The different values recorded in the literature for the rotation of *l*-arabinosazone and *l*-xylosazone are due to these substances showing mutarotation. F. B.

New Derivatives of Dextrose and Cellobiose. GÉZA ZEMPLÉN and EDUARD DESIDERIUS LÁSZLÓ (*Ber.*, 1915, **48**, 915—926).—The authors have prepared a number of penta-acyl derivatives of dextrose by the action of the acid chlorides of higher fatty acids, in the presence of dry pyridine, in very cold chloroform. Using acetobromodextrose and acetobromocellobiose, they have also prepared some mixed acyl compounds, by boiling them with silver salts in benzene.

*Penta*isovaleryl-β-dextrose, $C_6H_7O_6(C_5H_9O)_5$, forms very long, thin needles, m. p. 92°, $[\alpha]_D^{20}$ + 9·1°; *pentalauryl-α-dextrose*, $C_6H_7O_6(C_{12}H_{23}O)_5$, forms very long, slender needles, m. p. 52°, $[\alpha]_D^{20}$ + 40·62°; *pentalauryl-β-dextrose* crystallises in stellar aggregates of slender needles, m. p. 66°, $[\alpha]_D^{20}$ + 3·9°; *pentapalmityl-α-dextrose*, $C_6H_7O_6(C_{16}H_{31}O)_5$, has m. p. 75°, $[\alpha]_D^{20}$ + 29·7°, and *pentapalmityl-β-dextrose* forms microcrystalline spherules, m. p. 72°, $[\alpha]_D^{20}$ + 4·6° (compare a pentapalmityldextrose described by Stephenson, A., 1913, i, 952); *pentastearyl-β-dextrose*, $C_6H_7O_6(C_{18}H_{35}O)_5$, is a similar substance with m. p. 78°, $[\alpha]_D^{20}$ + 14·12°. These are all sparingly soluble in alcohol or water, but freely soluble in ether, light petroleum, or carbon disulphide.

The chlorocarbonic esters also reacted like the acyl chlorides. *Penta-methylcarbonato-β-dextrose*, $C_6H_7O_6(CO_2Me)_5$, forms microscopic, rhombic plates, m. p. 122—123°, $[\alpha]_D^{20}$ + 1·35°, and *pentaethylcarbonato-β-dextrose*, $C_6H_7O_6(CO_2Et)_5$, large columns or stout plates, m. p. 102°, $[\alpha]_D^{20}$ + 2·47°. These are sparingly soluble in ether, light petroleum, or carbon disulphide.

Benzoyltetra-acetyl-β-dextrose, $C_6H_7O_6BzAc_4$, from acetobromodextrose and silver benzoate, crystallises in glistening prisms, m. p. 146°, $[\alpha]_D^{20}$ − 28·1°; *salicyloyltetra-acetyl-β-dextrose*, $C_{21}H_{24}O_{12}$, forms prisms, m. p. 184°, $[\alpha]_D^{20}$ − 43·4°; and *hippuryltetra-acetyl-β-dextrose*, $C_6H_7O_6Ac_4{\cdot}CO{\cdot}CH_2{\cdot}NHBz$, separates in small needles, m. p. 193—194°, $[\alpha]_D^{20}$ + 3·64°. *Benzoylhepta-acetylcellobiose*, $C_{12}H_{14}O_{11}BzAc_7$, crystallises in thin needles, m. p. 210°, $[\alpha]_D^{20}$ − 30·5°; *salicyloylhepta-acetylcellobiose*, $C_{33}H_{40}O_{20}$, forms small needles, m. p. 221—223°, $[\alpha]_D^{20}$ − 43·43°; and *hippurylhepta-acetylcellobiose*, $C_{35}H_{43}O_{20}N$, yields slender needles, m. p. 186°, $[\alpha]_D^{20}$ − 15·04°.

All the rotations were observed in chloroform solutions.

J. C. W.

Existence of a Third Crystalline Penta-acetate of Galactose. C. S. HUDSON (*J. Amer. Chem. Soc.*, 1915, **37**, 1591—1593).—When galactose is acetylated with acetic anhydride and sodium acetate and

the product poured into cold water, the penta-acetate, m. p. 142°, separates. On extracting the water with chloroform and allowing the chloroform solution to evaporate slowly at the ordinary temperature, a further quantity of the same penta-acetate is obtained. The mother liquor from the latter yields crystals of another *galactose penta-acetate* which is not identical with that described by Hudson and Parker (following abstract), but has m. p. 98° and $[\alpha]_D^{20}$ -41·6° in chloroform. E. G.

Conversion of Galactose Penta-acetate into an Isomeric Form. C. S. HUDSON and H. O. PARKER (*J. Amer. Chem. Soc.*, 1915, **37**, 1589—1591).—Erwig and Koenigs (A., 1889, 1131) obtained a crystalline penta-acetylgalactose, m. p. 142°, by acetylating galactose with acetic anhydride and sodium acetate, and Fischer and Armstrong (A., 1902, i, 263) found that it has $[\alpha]_D$ +7·48° in benzene solution. These constants have now been confirmed, and determinations of $[\alpha]_D$ in chloroform solution have given the value + 25°.

When this penta-acetate is boiled with acetic anhydride and a little zinc chloride, a second crystalline *penta-acetate* is obtained in a yield of about 70% of the original form. This new penta-acetate has m. p. 95·5° and $[\alpha]_D^{20}$ about + 106·6° in chloroform, + 93·5° in benzene, + 113·6° in methyl alcohol, and + 114·0° in glacial acetic acid.

E. G.

The Action of Normal and Basic Lead Acetates on the Sugars, with Remarks on Rubner's Test for Dextrose and Lactose. HAROLD ROGERSON (*Biochem. J.*, 1915, **9**, 245—252).—The behaviour of the commonly occurring sugars towards normal and basic lead acetates under various conditions, with or without ammonia, sodium hydroxide or barium hydroxide, has been examined. It is found that sucrose is the only sugar which gives no manifestations of the development of colours or precipitates, and, therefore, Rubner's test for dextrose or lactose (A., 1885, 444), which depended on the formation of a reddish colour when the sugar is treated with lead acetate and sufficient ammonia to form a precipitate, should be abandoned. J. C. W.

Acetolysis of Carbohydrates. S. BORN and J. M. NELSON (*J. Amer. Chem. Soc.*, 1915, **37**, 1763—1769).—The authors' work on the constitution of invertase (A., 1914, i, 339) suggested that a study of the acetolysis of a number of disaccharides and polysaccharides might afford a clue to their structure and thus help to elucidate the constitution of the carbohydrate complex of invertase.

When sucrose is heated with acetyl bromide or chloride, acetylbromodextrose or acetylchlorodextrose is obtained. Maltose under similar conditions yields acetylbromomaltose and acetylchloromaltose; if this sugar is treated with acetic anhydride and sulphuric acid, it furnishes octa-acetylmaltose. By the action of acetyl chloride on lactose, a product is obtained which is probably acetylchlorolactose. When α-methylglucoside is treated with acetic anhydride and sulphuric acid, it yields α-penta-acetyldextrose. Acetyl bromide reacts with α-methyl-

glucoside with formation of a light brown, uncrystallisable syrup, and a similar result is obtained by the action of acetyl bromide on inulin.

The results of the experiments indicate that the different oxygen linkings in disaccharides and polysaccharides vary considerably in their stability towards acetolysis. E. G.

Action of Hydrogen Chloride on Carbohydrates. XV. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1915, **94**, 10—72).—It has recently been shown that many carbohydrates give rise to diastatically active substances when treated with hydrogen chloride followed by evacuation or exposure to ammonia (this vol., i, 325, 326). The separate action of these two gases on carbohydrates has therefore been made the subject of an investigation along the lines followed in the case of various enzymes (several papers in 1913). The experiments with hydrogen chloride are now described.

With the exception of lævulose and sucrose, which suffer considerable changes, even to charring, the carbohydrates examined, galactose, dextrose, maltose, lactose, starches and dextrin, form relatively simple additive compounds, which are decomposed by water, the hydrochloric acid being recovered completely. The weight of the gas absorbed varies considerably from case to case, and the increase in weight suffered by the powder is frequently more than the weight of the gas. The excess may be due to water, for the compounds are hygroscopic as a rule. When the products are evacuated, some of the hydrogen chloride is given up, but the solid still retains chlorine. The final substance often weighs less than the original, dry carbohydrate, showing that something besides hydrogen chloride is lost on evacuation. This, again, may be water, but the excess loss of weight has not the relation to the remaining chlorine that any reaction involving the formation of a chloride would warrant. It may be that some of the loss is due to volatile organic halogen compounds, although experiments in this connexion have not been devised. J. C. W.

Preparation of Methylglycocyamidine (Creatinine). FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 281051; from *J. Soc. Chem. Ind.*, 1915, **34**, 637).—A quantitative yield of creatinine is obtained by heating *N*-methylglycocyamine (methylguanidoacetic acid) with an organic acid. J. C. W.

Nitration of Methylcarbamide. H. J. BACKER (*Rec. trav. chim.*, 1915, **34**, 187—203).—The author has repeated the work of Degner and von Pechmann (A., 1897, i, 264) on the nitration of methylcarbamide, and finds that the product of the reaction is not one substance as they state but a mixture of two isomeric nitromethylcarbamides: $NO_2 \cdot NMe \cdot CO \cdot NH_2$ and $NHMe \cdot CO \cdot NH \cdot NO_2$. The constitution of their compound, m. p. 159°, is more correctly represented by the second formula, and not the first, as stated by them.

When methylcarbamide nitrate is slowly added to concentrated sulphuric acid at −15°, a nitrated product, m. p. 90—100° (decomp.), is obtained. When this product is dissolved in aqueous ammonia and reprecipitated by dilute sulphuric acid, 55% of it is recovered as α-nitro-γ-methylcarbamide, m. p. 159°. The remainder consists of its

isomeride, *α*-nitro-*α*-methylcarbamide. The compound, m. p. 159°, on reduction gives methylsemicarbazide, $NHMe\cdot CO\cdot NH\cdot NH_2$, from which have been prepared benzaldehyde methylsemicarbazone, m. p. 166°; *salicylaldehyde methylsemicarbazone*,

$$HO\cdot C_6H_4\cdot CH{:}N\cdot NH\cdot CO\cdot NHMe;$$

anisaldehyde methylsemicarbazone, $C_{19}H_{13}O_2N_3$, m. p. 175°; *piperonal methylsemicarbazone*, $C_{10}H_{11}O_3N_3$, white needles, m. p. 203·5°; and *p-nitrobenzaldehyde methylsemicarbazone*, $C_9H_{10}O_3N_4$, yellow needles, m. p. 236°, which is transformed by concentrated hydrochloric acid into a white powder. Methylsemicarbazide condenses with acetylacetone, giving 3 : 5-*dimethylpyrazole*-1-*carboxymethylamide*,

$$NHMe\cdot CO\cdot N\begin{matrix}N{=\!=}CMe\\ CMe{:}CH\end{matrix},$$

m. p. 71°. It is volatile with steam, and when warmed with 10% aqueous potassium hydroxide gives 3 : 5-dimethylpyrazole.

(W. Stortenbeker.—The first-named pyrazole crystallises from light petroleum in small, rhombic crystals; $a : b : c = 0{\cdot}755 : 1 : 0{\cdot}546$.)

The nitromethylcarbamide, m. p. 159°, when warmed with aqueous potassium hydroxide, evolves nitrous oxide, and with barium hydroxide gives nitrous oxide, barium carbonate, and methylamine,

$$NHMe\cdot CO\cdot NH\cdot NO_2 + Ba(OH)_2 = CH_3\cdot NH_2 + BaCO_3 + N_2O + H_2O.$$

When heated with aqueous ammonia in a sealed tube at 100° it yields methylcarbamide and nitrous oxide,

$$NHMe\cdot CO\cdot NH\cdot NO_2 + NH_3 = NHMe\cdot CO\cdot NH_2 + N_2O + H_2O.$$

The crude nitration product, m. p. 90—100°, when heated with aqueous potassium hydroxide gives nitrous oxide, as above, and a small amount of an inflammable gas, arising from the decomposition of the methylnitroamine formed. With barium hydroxide, in addition to the products from the isomeride, m. p. 159°, methylnitroamine was isolated as a product from the other isomeride,

$$2NO_2\cdot NMe\cdot CO\cdot NH_2 + 3Ba(OH)_2 = (NMe\cdot NO_2)_2Ba + 2BaCO_3 + 2NH_3 + 2H_2O.$$

Similarly with ammonia, the second isomeride gave the reaction

$$NO_2\cdot NMe\cdot CO\cdot NH_2 + 2NH_3 = NO_2\cdot NMe\cdot NH_4 + CO(NH_2)_2.$$

Attempts to synthesise *α*-nitro-*α*-methylcarbamide by the methylation of nitrocarbamide by methyl iodide, diazomethane or methyl sulphate were not successful. Nitration of methylacetylcarbamide resulted in its decomposition when nitric acid was the nitrating agent:

$$NHAc\cdot CO\cdot NHMe + 3HNO_3 = CH_3\cdot CO_2H + CH_3\cdot O\cdot NO_2 + CO_2 + 2N_2O + 2H_2O.$$

Ethyl nitrate was without action on this substituted carbamide.

W. G.

Preparation of an Organic Peroxide Compound (Tetramethylenedicarbamide Diperoxide). C. von Girsewald (D.R.-P. 281045; from *J. Soc. Chem. Ind.*, 1915, **34**, 636).—An addition to D.R.-P. 263459 (A., 1914, i, 19). Hydrogen peroxide, in the presence of an acid, is treated with carbamide and formaldehyde, instead of with hexamethylenetetramine. The new *compound*,

$$O_2(CH_2\cdot NH\cdot CO\cdot NH\cdot CH_2)_2O_2,$$

is stable, and may be used as a germicide. J. C. W.

Preparation of α-Bromo-α-ethylbutyrylcarbamide. FARBENFABRIKEN VORM. F. BAYER & Co. (Third addition to Fr. Pat. 417803; from *J. Soc. Chem. Ind.*, 1915, **34**, 512).—*α-Ethylbutyrylcarbimide*, $CHEt_2{\cdot}CO{\cdot}N{:}CO$, b. p. 55°/23 mm., prepared by heating α-ethylbutyryl chloride with mercuric cyanate, is treated with bromine, followed by ammonia, and so converted into α-bromo-α-ethylbutyrylcarbamide, $CBrEt_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$ (A., 1911, i, 118). J. C. W.

Derivatives of Diaminoguanidine. AUGUSTO GAITER (*Gazzetta*, 1915, **45**, i, 450—461).—The fact that the aminoiminic group, $:N{\cdot}NH_2$, certainly exists in the molecule of triaminoguanidine, which is very readily formed, leads to the supposition that it may occur also in diaminoguanidine (compare Pellizzari and Cantoni, A., 1905, i, 576; Pellizzari and Gaiter, A., 1914, i, 1054). For aminoguanidine, Thiele gives the iminic formula, whilst, owing to the formation from it of 3 : 6-diamino-1 : 2 : 4 : 5-tetrazine, Ponzio and Gastaldi (A., 1913, i, 1109) assumed that it reacts according to the hydrazonic structure. It may, therefore, be that diaminoguanidine exists in the two forms, $NH{:}C(NH{\cdot}NH_2)_2$ and $NH_2{\cdot}N{:}C(NH_2){\cdot}NH{\cdot}NH_2$, but no verification of the second of these formulæ has yet been obtained; that the first holds good is shown by the reaction with benzoyl chloride, which yields a di- and a tetra-benzoyldiaminoguanidine, giving two mols. of *s*-dibenzoylhydrazine on hydrolysis:

$$NH{:}C(NH{\cdot}NH_2)_2 \longrightarrow NH{:}C(NBz{\cdot}NHBz)_2,$$

and this $+2H_2O = CO_2 + NH_3 + 2NHBz{\cdot}NHBz$.

Like aminoguanidine, diaminoguanidine forms additive products, $NH{:}C(NH{\cdot}N{:}CHR)_2$, with aliphatic and aromatic aldehydes, and reacts with organic acids to form aminated triazole nuclei. Whilst free diaminoguanidine cannot be isolated owing to its ready solubility and the ease with which it undergoes change, its condensation products with benzaldehyde, salicylaldehyde, *m*-nitrobenzaldehyde, and glyoxal are readily separable in the crystalline form; they retain the properties of guanidine derivatives and exhibit basic properties. The additive compound with glyoxal is formed with one molecule of the base, and therefore probably represents a 7- or 6-membered closed ring, according as the diaminoguanidine acts in the ordinary or in the desmotropic hydrazonic form; the data at present available do not decide this question.

Salts of diaminoguanidine (1 mol.) also react with formic acid and its homologues (1 mol.), elimination of 2 mols. of water leading to the formation of the salt of a base which is certainly of closed-ring structure. The reaction takes place in two phases, the first giving a monoformyl derivative, which cannot, however, be separated, as it immediately loses a second molecule of water: $NH{:}C(NH{\cdot}NH_2)_2 \longrightarrow NH{:}C(NH{\cdot}NH_2){\cdot}NH{\cdot}NH{\cdot}CHO \longrightarrow C_2H_5N_5$. The chemical behaviour of the final product indicates that it is, not a derivative of a six-membered ring, but a triazole derivative, $NH{:}C\langle^{NH\text{——}N}_{N(NH_2){\cdot}CH}$, since with benzaldehyde it forms a condensation product containing an amino-group, and since with nitrous acid it yields a nitroso-derivative

identical with that of Thiele and Manchot's aminotriazole (A., 1899, i, 167): $NH{:}C<^{NH\text{——}N}_{N(NH_2)\cdot CH}$ + HNO_2 → $NH{:}C<^{NH\cdot N}_{NH\cdot CH}$ + HNO_2 → $C_2H_3N_4\cdot NO$. This triazole derivative may have either the formula given above or the tautomeric formula,

$$NH_2\cdot C<^{N\text{———}N}_{N(NH_2)\cdot CH};$$

preference is given to the former because the compound condenses with 1 mol. only of an aldehyde, but it is probable that it reacts according to both structures.

Disalicylidenediaminoguanidine, $NH{:}C(NH\cdot N{:}CH\cdot C_6H_4\cdot OH)_2$, forms shining, yellow prisms, m. p. 201—203°, and is obtained as *hydrobromide*, $C_{15}H_{15}O_2N_5,HBr$, m. p. 240°, from diaminoguanidine hydrobromide (1 mol.) and salicylaldehyde (2 mols.). *Di-m-nitrobenzylidenediaminoguanidine*, $NH{:}C(NH\cdot N{:}CH\cdot C_6H_4\cdot NO_2)_2$, forms minute, yellow crystals, m. p. 240—242°, and its *hydrobromide* a yellow, pulverulent precipitate, gradually reddening in the air, m. p. 292° (decomp.). *Dibenzoyldiaminoguanidine*,

$$NH{:}C(NH\cdot NHBz)_2,$$

forms nacreous, dendritic masses or minute scales, m. p. 210—211°. *s-Tetrabenzoyldiaminoguanidine*, $NH{:}C(NBz\cdot NHBz)_2$, forms a white, curdy precipitate or, when dry, a shining, crystalline powder, m. p. 169°.

4-Amino-5-iminodihydro-1 : 2 : 4-triazole, $NH{:}C<^{N(NH_2)\cdot CH}_{NH\text{——}N}$, obtained as hydrobromide from diaminoguanidine (1 mol.) and formic acid (1 mol.), forms pale yellow needles, m. p. 208°. The following derivatives were prepared: *hydrobromide*, m. p. 216—218°, decomposing at a higher temperature; *picrate*, $C_2H_5N_5,C_6H_3O_7N_3$, m. p. 192°; and *nitrate*, $C_2H_5N_5,HNO_3$, m. p. 194°, decomposing at a higher temperature. *4-Benzylideneamino-5-iminodihydro-1 : 2 : 4-triazole*,

$$NH{:}C<^{N(N{:}CHPh)\cdot CH}_{NH\text{————}N},$$

forms shining, yellow plates, m. p. 235—236°. *4-Amino-5-imino-3-methyldihydro-1 : 2 : 4-triazole*, $NH{:}C<^{N(NH_2)\cdot CMe}_{NH\text{——}N}$, obtained as *nitrate*, m. p. 184°, from diaminoguanidine nitrate, acetic acid and nitric acid, forms needles, m. p. 193°. The *picrate*, $C_3H_7N_5,C_6H_3O_7N_3$, m. p. 189° (decomp.), and *platinichloride*, $C_3H_7N_5,H_2PtCl_6$, m. p. 226°, were prepared. T. H. P.

Conversion of Cyanamide into Ammonia. F. Löhnis (*Chem. Zentr.*, 1915, i, 567; from *Zeitsch. Gärungsphysiol.*, 1915, **5**, 16—25).—The direct formation of ammonia from calcium cyanamide or cyanamide is favoured by an acid medium and effected chiefly by moulds, not by bacteria. Suitable moulds, belonging mainly to the *Penicillium* class, are probably present in all soils. Only a portion of the cyanamide decomposed is actually converted into ammonia, however, whereas in the soil a practically quantitative conversion is effected. It seems

probable, therefore, that the colloids of the soil are the chief agents in causing the primary transformation into carbamide. H. W.

The Auto-oxidation of Lipoid Substances, and the Nature of Certain Pigments (Chromolipoids) and Pigment Complexes. C. Ciaccio (*Biochem. Zeitsch.*, 1915, **69**, 313—333).—Certain unsaturated fatty substances such as oleic and linoleic acids, and various lipoids, such as lecithin and the brain lipoids, undergo auto-oxidation, which produces changes in the colour, consistency, solubility, and behaviour towards acids and bases, but retain at the same time their characteristic behaviour towards certain reagents for fats. The properties of the oxidation products are similar to those of the fatty pigments or lipofuscins. The auto-oxidation is accelerated by iron, manganese, and magnesium. These oxidation products can be separated into two classes, viz., the chromolipoids derived from the phosphatides, and those derived from fatty acids. An account is given of the differences of the behaviour of the various chromolipoids towards staining reagents such as Soudan-red III, Scarlet-R, and the reagents of Fischler, and of Smith-Dietrich. S. B. S.

Preparation of Lipoid Phosphorus Compounds of Derivatives of Higher Fatty Acids. F. Hoffmann-La Roche & Co. (D.R.-P. 280411; from *J. Soc. Chem. Ind.*, 1915, **34**, 452).—The higher ketonic aliphatic acids, or such derivatives as the esters, amides, diketonic acids or hydroxyketonic acids, are treated with hypophosphorous acid or its salts. The new acids are sparingly soluble in water, form readily soluble alkali and ammonium salts, and are quite stable towards bases. They are readily resorbed, and are powerful reducing agents. J. C. W.

Preparation of Boroformates. H. Weitz (Fr. Pat. 472233; from *J. Soc. Chem. Ind.*, 1915, **34**, 424).—A hydroxide or carbonate of an alkali or alkaline earth is dissolved in water in the presence of boric and formic acids, or their soluble alkali or alkaline earth salts. Thus, the *sodium boroformate*, $NaH_4CBO_5,2H_2O$, is prepared by adding concentrated formic acid to a solution containing borax and sodium carbonate. J. C. W.

Isomerisation of Cyclic Compounds. N. A. Rosanov (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 591—610).—Results obtained by various investigators may be expressed in the following general rules: Rings, of whatever type they may be, exhibit instability towards certain reagents, such instability being independent of the tension described by Baeyer. Further, isomerisation of ring compounds usually proceeds in such a manner that cyclic compounds containing a side-chain are transformed into larger rings, whilst those without side-chains give smaller rings with side-chains.

Investigation of the absorption spectra of cyclic nitro-compounds obtained by Meyer's method (compare Zelinski and Rosanov, A., 1911, ii, 1044) shows that this reaction not only proceeds in the direction of replacement of a halogen atom by the nitro-group, but is accompanied by isomerisation of the ring, tertiary or primary nitro-derivatives, or,

in some cases, hydrocarbons, being obtained in place of the secondary nitro-compounds expected. Such isomerisation is observed in the preparation of nitro-compounds from halogen derivatives of *cyclo*pentanol, 3-methyl*cyclo*pentanol, 2-, 3- and 4-methyl*cyclo*hexanols, and 2-, 3- and 4-methyl*cyclo*hexylcarbinols.

The author has made further experiments on the isomerisation of *cyclo*pentanol derivatives. Reduction of *cyclo*pentyl iodide by means of zinc dust and acetic acid yields *cyclo*pentane, which is shown to be identical with the synthetic hydrocarbon by comparison of the ultra-violet absorption curves. The curve which Zelinski and Lisicin (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 324) regard as that of methyl*cyclo*butane differs markedly from the curve for *cyclo*pentane, and exhibits a maximum absorption band at $1/\lambda = 4450$; the author considers it probable that this curve is that of a mixture of hydrocarbons, including *cyclo*pentene.

Treatment of *cyclo*pentyl iodide with silver nitrite in ethereal solution yields (1) nitric oxide and hydrogen cyanide; (2) a small proportion of a hydrocarbon, C_5H_8, probably methylene*cyclo*butane, and (3) *cyclo*pentyl nitrite. Treatment of the latter with concentrated alkali hydroxide solution yields (1) a small proportion of the secondary nitro-compound; (2) *cyclo*pentanol; (3) 1-*nitro*-1-*methyl*cyclo*butane*, $CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>CMe\cdot NO_2$, b. p. 80—82°/30 mm., n_D^{20} 1·4589, D_4^{20} 1·0795, and (4) the ψ-nitrole, $\begin{matrix}CH_2\cdot CH_2\\|\\CH_2\cdot CH_2\end{matrix}>C(NO)\cdot NO_2$ (compare Demjanov, A., 1910, i, 838); the same products, with the exception of *cyclo*pentanol, are obtained when *cyclo*pentyl nitrite is treated with sodium ethoxide.

Conversion of *cyclo*pentylcarbinol into iodomethyl*cyclo*pentane and treatment of the latter with silver nitrite gives (1) principally 1-nitro-1-methyl*cyclo*pentane; (2) *ω-nitromethyl*cyclo*pentane*,

$$\begin{matrix}CH_2\cdot CH_2\\|\\CH_2\cdot CH_2\end{matrix}>CH\cdot CH_2\cdot NO_2,$$

which is a colourless liquid, b. p. 110°/35 mm., giving intensely yellow solutions in alkali hydroxide solutions, and (3) traces of nitro*cyclo*hexane.

The action of oxalic acid on *cyclo*pentylcarbinol yields *cyclo*hexene, the bicyclic compound, $CH_2<\begin{matrix}CH_2\cdot CH\\|\\CH_2\cdot CH\end{matrix}>CH_2$, being probably formed as an intermediate product.

These results render evident the lability of five-membered rings, which, according to Baeyer's tension hypothesis, should exhibit marked stability. Such capacity for isomerisation is revealed not merely under the action of acid reagents, but also in such a mild reaction as nitration by means of silver nitrite. The general rules enunciated above are observed in the cases investigated by the author. T. H. P.

Preparation of Aromatic Chloro-compounds. Kinzlberger & Co. (D.R.-P. 280739; from *J. Soc. Chem. Ind.*, 1915, **34**, 543).—Aromatic nitro-compounds are heated with thionyl chloride at above

160°. The nitro-groups, and also sulpho-groups and hydrogen atoms of aliphatic side-chains, are replaced by chlorine. The application to nitrobenzene, *p*-nitrotoluene, and dinitroanthraquinone is described.

J. C. W.

Nitration of Mixed Dihalogenbenzenes. A. F. Holleman (*Rec. trav. chim.*, 1915, **34**, 204—234).—For the most part a résumé of work already published (this vol., i, 59).

[With Heineken.]—*p*-Fluorochlorobenzene, $n^{15} = 1{\cdot}4990$, was prepared by diazotisation of *p*-fluoroaniline. Attempts to prepare a nitro-derivative were unsuccessful, the only product being 4-chloro-2 : 6-dinitrophenol, m. p. 82°. *p*-Fluorobromobenzene, n^{15} 1·5310, was also prepared from *p*-fluoroaniline. This substance on nitration gave 4-bromo-2 : 6-dinitrophenol, m. p. 75°, together with an oil which was shown to contain 1-fluoro-4-bromo-3-nitro- and 1-fluoro-4-bromo-2-nitrobenzene. Decomposition with sodium methoxide in a sealed tube and estimation of the sodium bromide formed showed that the oil contained 30·5% of 1-fluoro-4-bromo-3-nitrobenzene. W. G.

Aromatic Nitro-derivatives. IV. Solubility of Certain Nitro-derivatives of Toluene and Benzene in the Solid State. Michele Giua (*Gazzetta*, 1915, **45**, i, 557—566. Compare A., 1914, i, 817).—The author has submitted the following binary systems to thermal analysis.

2 : 4 : 6-Trinitrotoluene and 2 : 4 : 5-trinitrotoluene form an additive compound containing 3 mols. of the former and 2 mols. of the latter. The eutectic between the 2 : 4 : 6-derivative and this compound melts at 56·75° and that of the compound and 2 : 4 : 5-trinitrotoluene at 58·2°.

p-Nitrotoluene and 2 : 6-dinitrotoluene give a melting-point curve in which the part parallel to the axis of concentration is very restricted, so that thermal analysis does not permit of the determination of the composition of the compound from the thermal arrests. For 3 mols. of the mono- and 2 of the di-nitrotoluene, the melting point of the compound coincides with that of the eutectic between the compound and the *p*-nitrotoluene.

In the system *p*-nitrotoluene–2 : 4 : 6-trinitrotoluene, it is possible to delimit experimentally the metastable region. The part of the curve parallel to the concentration axis stretches over about 5% and indicates the formation of a compound of 3 mols. of *p*-nitrotoluene and 2 mols. of the trinitrotoluene.

In the system 2 : 4 : 6-trinitrotoluene–*m*-dinitrobenzene, there is an indication over a limited concentration of the formation of an additive compound, dissociating into its components in the liquid state.

With *p*-nitrotoluene–*m*-dinitrobenzene, the two curves meet in a eutectic point at 29·5°, but the corresponding eutectic has two solidification points. Similar behaviour is shown by the system containing 2 : 4-dinitrotoluene and *m*-dinitrobenzene.

The system *p*-nitrotoluene–diphenylamine exhibits a eutectic solidifying at 18·5°. All the mixtures investigated show in the hot a reddish-yellow colour, which is produced by even a small proportion of the nitro-compound. T. H. P.

Polymerisation of Styrene. II. HANS STOBBE (*Annalen*, 1915, **409**, 1—13. Compare A., 1910, i, 235).—With regard to the polymerisation of styrene to metastyrene, the three conclusions previously drawn from the results of viscosity measurements (*loc. cit.*) have been confirmed by means of the change of the refractive index with time; the refractive index of styrene is measurably increased by the presence of a very small amount of metastyrene.

It has been found that not only light but also heat stimulates the transformation; under the same conditions, samples of styrene which have been previously heated and exposed to light polymerise more rapidly than others which have not been so treated.

The tendency to polymerisation is greater in stored than in freshly distilled samples of styrene. C. S.

Electrolytic Formation of Hydrocarbons from Salts of Pure Aromatic Carboxylic Acids. C. SCHALL (*Zeitsch. Elektrochem.*, 1915, **21**, 69—73).—The electrolysis of *p*-nitrobenzoic acid and its potassium salt in solution in boiling acetic anhydride has been carried out both with and without diaphragms, using a current of 0·4 ampere and 22—25 volts. At the cathode the only product was hydrogen, whilst at the anode, carbon dioxide, carbon monoxide, hydrocarbons of the C_nH_{2n} series, oxygen, methane and ethane together with exceedingly small quantities of 4 : 4′-dinitrodiphenyl were produced. The presence of the dinitrodiphenyl was proved by its conversion into benzidine. The formation of dinitrodiphenyl is analogous to the formation of ethane from potassium acetate, and its formation is to be regarded as electrolytic and not thermal. Side reactions take place in the electrolysis with the formation of nitrobenzene and deep brown substances. J. F. S.

Halogen Derivatives of Hydrocarbons of the Diphenylmethane Series. A. M. NASTJUKOV and V. F. ANDRÉEV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 552—558).—By means of the method suggested by Nastjukov (A., 1904, i, 242; 1909, i, 19) for the preparation of diphenylmethane from benzene and ditolylmethane from toluene, the authors have prepared the following new chloro-derivatives of the diphenylmethane series.

Dichlorodiphenylmethane, $CH_2(C_6H_4Cl)_2$, prepared either from chlorobenzene, concentrated sulphuric acid and formaldehyde or by dry distillation of the corresponding formolite yielded by the interaction of these compounds, is an almost colourless liquid with a faint, pleasant odour and slight fluorescence, b. p. 317—318°, D_{21}^{21} 1·2336, $n_D^{19·6}$ 1·5948, and has the normal molecular weight in freezing benzene; in a cooling mixture it forms a solid mass, m. p. about 8°. When oxidised by means of chromyl chloride, it yields a *dichlorobenzophenone*, m. p. 126—127°, which gives an *oxime*, m. p. 132—133°. The compound is not identical with either 2 : 2′-dichlorodiphenylmethane (compare Norris and Twieg, A., 1904, i, 63) or 4 : 4′-dichlorodiphenylmethane, since 4 : 4′-dichlorodibenzophenone has m. p. 144·5° (compare Norris and Green, A., 1902, i, 379; Montagne, A., 1902, i, 472). On the assumption that it possesses a symmetrical formula, the compound is regarded as 3 : 3′-dichlorodiphenylmethane.

In a similar manner, *o*-chlorotoluene, sulphuric acid, and formaldehyde give a *dichloroditolylmethane*, $CH_2(C_6H_3MeCl)_2$, which is a colourless liquid, b. p. 340—343°, D_{20}^{20} 1·2232, $n_D^{19·7}$ 1·5900, and has the normal molecular weight in freezing benzene; the corresponding *dichloroditolyl ketone*, $CO(C_6H_3MeCl)_2$, has m. p. 132—133°.

The isomeric *dichloroditolylmethane* obtained by this method from *p*-chlorotoluene forms flat, colourless needles, m. p. 42°, b. p. 205°/20 mm., and exhibits normal cryoscopic behaviour in benzene.

With *p*-dichlorobenzene the reaction does not take place.

T. H. P.

Disposition of the Bonds of the Quinquevalent Nitrogen Atom. I. J. B. Cohen, J. Marshall, and H. E. Woodman (T., 1915, **107**, 887—902).—An attempt has been made to decide between the double tetrahedron arrangement of Willgerodt and the pyramid formula of Bischoff by preparing a quaternary ammonium compound NR_3R^+X (R^+ = active radicle) from NR_3 and R^+X and also from NR_2R^+ and RX. Identity in rotatory power of the two products would indicate the correctness of the symmetric formula of Bischoff, and lack of identity would favour Willgerodt's formula. This was effected in the case of l-*γ-phenylbutyltriethylammonium bromide*, and the products were apparently identical, having $[\alpha]_D^{20}$ −7·0° and −7·5° respectively. Attempts to obtain a more rigid proof by preparing a compound of the type $NR_2R^+R^-X$ from a tertiary base containing one enantiomorphous radicle, R^+, and an alkyl haloid containing the other, R^-, in which case, according to Bischoff, the product would be inactive by internal compensation, but, according to Willgerodt, optically active, have not yet been brought to a conclusion owing to the difficulty in obtaining the two enantiomorphous forms of a suitable alcohol in quantity. A proof that the introduction of enantiomorphous radicles into symmetrical positions in a molecule formed an inactive substance was afforded by the preparation of *succinyl-* and *methylsuccinyl-bornylamides*, containing *d-* and *l*-bornyl radicles; the former, m. p. 242—243°, was inactive, and the latter, m. p. 229—230°, gave $[\alpha]_D^{18} \pm 3·4°$ (in alcohol).

The following substances were prepared, and the alcohols were in some cases resolved by fractionally crystallising the salts of the hydrogen esters of phthalic acid with active alkaloids. Resolution of *dl-sec.*-butylcarbinol was not complete, as the acid nitrophthalic ester, $[\alpha]_D^{20} \pm 2·65°$, suffered partial racemisation on hydrolysis. *Phenyl-p-tolylcarbinol* forms prisms, m. p. 57°. *Phenyl-p-tolylmethylamine* was resolved by fractional crystallisation of the bromocamphorsulphonate, and the corresponding l-*phenyl-p-tolylcarbinol* had $[\alpha]_D^{20}$ −1·4°. *β*-Phenylpropyl alcohol forms a *benzoate*, b. p. 218—220°/15 mm., *p-nitrobenzoate*, m. p. 65°, *hydrogen phthalate*, m. p. 79°, and *hydrogen 3-nitrophthalate*, m. p. 147°. The alcohol was resolved by means of the nitrophthalate, and the products obtained by hydrolysis of the active esters had $[\alpha]_D^{20}$ +15·25° and −15·16°. *β-Phenylpropyl bromide* boils at 106—108°/18 mm., $[\alpha]_D^{20} \pm 15·6°$. dl-*γ-Phenylbutyl alcohol* boils at 138—140°/33 mm., and the *l*-alcohol, $[\alpha]_D^{20}$ −35·2°, forms a *bromide*,

b. p. 120°/16·5 mm., $[\alpha]_D^{20} - 72{\cdot}8°$. l-γ-*Phenylbutyldiethylamine* boils at 152°/38 mm., and has $[\alpha]_D^{20} - 27{\cdot}75°$. G. F. M.

Nitration of the Anilides of Halogen-substituted Acids. Emil Votoček and Jan Burda (*Ber.*, 1915, **48**, 1002—1008).—In the nitration of the anilides of organic acids, the best known examples being acetanilide and benzanilide, it has been generally observed that the substituent group enters exclusively at the ortho- and para-positions to the amino-radicle. The authors have now investigated the effect of the presence of a halogen element in the acid constituent, and find that the behaviour on nitration is still the same. The anilides examined were those derived from the three chloroacetic acids and were prepared by interaction of the acid and aniline (2 mols.) in benzene solution. Nitration was effected by introducing the anilide into excess of cold fuming nitric acid (94%).

Chloroacetanilide, m. p. 135°, was converted into *p*-nitrochloroacetanilide, $CH_2Cl{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$, m. p. 185—185·5° (Deutsch [A., 1907, i, 1082] gives 151°); this substance was accompanied by *o-nitrochloroacetanilide*, m. p. 90—93°. The position of the nitro-group in these substances and also in those mentioned below was proved by hydrolysis to the corresponding nitroanilines. The above *o*-nitrochloroacetanilide was also synthesised directly from the constituent acid and base.

Dichloroacetanilide, m. p. 118—121°, on nitration yielded p-*nitrodichloroacetanilide*, $CHCl_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$, m. p. 147—148·5°, together with the isomeric o-*nitrodichloroacetanilide*, yellow crystals, m. p. 78—80°.

Trichloroacetanilide, m. p. 95—97°, when nitrated produced *p*-nitrotrichloroacetanilide, and o-*nitrotrichloroacetanilide*, a yellow solid, m. p. 70—72°.

Repetition of the nitration of chloroacetanilide and trichloroacetanilide in solution in cold sulphuric acid gave the same products as were obtained in the absence of the sulphuric acid, the meta-substituted anilide being absent in both cases.

The suggestion is made that it is not the degree of the negative character of the acyl group which decides the position to be assumed by the substituent group, and that the difference between the behaviour of aniline and the anilides on nitration is due to the nitrogen atom being quinquevalent in the former and tervalent in the latter during the chemical change. D. F. T.

Quaternary Salts of Hexamethylenetetramine. I. Substituted Benzyl Haloids and the Hexamethylenetetraminium Salts Derived Therefrom. Walter H. Jacobs and Michael Heidelberger (*J. Biol. Chem.*, 1915, **20**, 659—683).—In this and the following papers the authors give an account of the preparation and properties of a large number of quaternary ammonium compounds of the general formula $C_6H_{12}N_4{\cdot}RX$, produced by the combination of hexamethylenetetramine with substituted benzyl haloids and halogen-acetyl derivatives of aliphatic and aromatic amines. These compounds represent a new group of organic bactericides, the biological

investigation of which will be described in a subsequent communication. They were all prepared by heating molecular proportions of hexamethylenetetramine and the requisite halogen derivative in chloroform solution. Those containing aromatic radicles undergo decomposition in aqueous solution with liberation of formaldehyde and the separation of a product as a colloidal suspension, an emulsion of oil drops or a crystalline precipitate, depending on the salt used. These precipitates are usually soluble in acids, and where isolation was possible, have been shown to consist principally of the methylene compounds of the corresponding primary amines.

The following compounds derived from substituted benzyl haloids are described:

o-*Methylbenzylhexamethylenetetraminium chloride*, $C_{14}H_{21}N_4Cl$, diamond-shaped micro-plates, m. p. 202—204°, with preliminary darkening and softening; the corresponding m-*compound* has m. p. 204—205° (decomp.), with previous darkening; the p-*isomeride* sinters and turns yellow at 186°, m. p. 198°; 3 : 5-*dimethylbenzylhexamethylenetetraminium chloride*, m. p. 203—204° (decomp.); o-*xylylenedihexamethylenetetraminium dichloride*, $C_{20}H_{32}N_8Cl_2$, decomp. 162°, from *o*-xylylene dichloride; m-*xylylenedihexamethylenetetraminium dichloride*, m. p. 180—186°; *mesityldihexamethylenetetraminium dichloride*, m. p. 188—191° (decomp.); *β-naphthylmethylhexamethylenetetraminium chloride*, m. p. 190—195° after turning yellow; o-*chlorobenzylhexamethylenetetraminium chloride*, minute, glistening plates, m. p. 201—203° (decomp.); p-*chlorobenzylhexamethylenetetraminium chloride*, micro-prisms, m. p. 202—205° (decomp.).

o-*Bromobenzyl chloride*, prepared by passing chlorine into boiling *o*-bromotoluene, has b. p. 124—126° (corr.)/20 mm., and yields a hexamethylenetetramine *compound*, m. p. 183—186° (decomp.); p-*bromobenzylhexamethylenetetraminium chloride*, micro-crystals, m. p. 192° (decomp.); p-*iodobenzylhexamethylenetetraminium bromide*, m. p. 181—182° (decomp.); o-*cyanobenzylhexamethylenetetraminium chloride*, stout, irregular micro-plates, m. p. 183° (decomp.) with preliminary darkening; p-*cyanobenzylhexamethylenetetraminium chloride*, glistening micro-plates, m. p. 193—193·5° (decomp.); o-*nitrobenzylhexamethylenetetraminium chloride* becomes orange at 175—176°, decomp. 178—179°; the corresponding m-*compound*, glistening micro-prisms, has m. p. 199—202° (decomp.); the p-*isomeride*, m. p. 173—174° (decomp.).

p-Nitrobenzylpyridinium chloride forms almost colourless, diamond-shaped prisms, softening at 203°, and melting at 204—207° to a red liquid; Lellman and Pekrun (A., 1891, 88) give m. p. 103°.

2 : 4-*Dinitrobenzylhexamethylenetetraminium chloride* crystallises in faintly yellow micro-platelets, m. p. 178—179° (decomp.).

o-*Acetylaminobenzylhexamethylenetetraminium chloride* forms micro-platelets, m. p. 180—182° (decomp.); the p-*isomeride*, micro-prisms, m. p. 175—177° (decomp.).

3-Nitro-4-hydroxybenzylpiperidine, prepared from 3-nitro-4-hydroxybenzyl chloride and piperidine in boiling alcoholic solution, crystallises in orange-brown needles, m. p. 141—143°, with preliminary softening (compare Auwers and Dombrowski, A., 1906, i, 380), and on treatment with acetyl chloride in pyridine solution is converted into

3-*nitro*-4-*acetoxybenzylpiperidine hydrochloride*, faintly yellow, glistening micro-platelets, m. p. 178—179°; it is reduced by stannous chloride and hydrochloric acid to 3-*amino*-4-*hydroxybenzylpiperidine dihydrochloride*, microscopic, hexagonal plates, which soften at 135° and evolve gas at 180°.

2-*Acetoxy*-3 : 5-*dimethylbenzyl chloride*, prepared by heating 2-hydroxy-3 : 5-dimethylbenzyl chloride with acetic anhydride and a little sulphuric acid, has b. p. 160—170°/12 mm., m. p. 37·5—38° (corr.), with slight preliminary softening, and yields a hexamethylenetetramine *compound*, m. p. 158°.

3 : 5-*Dibromo*-2-*hydroxybenzylhexamethylenetetraminium bromide* becomes yellow above 165°, m. p. 173—174°; 3 : 5-*dibromo*-2-*acetoxybenzylhexamethylenetetraminium bromide* gradually softens above 135° (decomp. 151—153°); 3 : 5-*dibromo*-4-*acetoxybenzylhexamethylenetetraminium bromide*, m. p. 184—185° with previous sintering at 180°; 4 : 6-*dibromo*-2-*acetoxy*-3 : 5-*dimethylbenzylhexamethyl-netetraminium bromide*, m. p. 150—151°; 5-*nitro*-2-*hydroxybenzylhexamethylenetetraminium chloride*, bright yellow powder, m. p. 210° (decomp.).

3-*Nitro*-4-*acetoxybenzyl chloride*, prepared by acetylating the corresponding hydroxy-compound, forms faintly yellow, glistening leaflets, m. p. 59·5—60° (corr.), and is converted by sodium iodide in acetone solution into 3-*nitro*-4-*acetoxybenzyl iodide*, almost colourless, slender needles, m. p. 65·5—68° (corr.), which yields a hexamethylenetetramine *compound*, softening at 159° to a semi-fluid, orange-coloured mass.

3-*Nitro*-6-*acetoxybenzyl chloride*, obtained in a similar manner, separates from alcohol in minute, colourless platelets, having the composition $C_9H_8O_4NCl,Et{\cdot}OH$; it softens above 55° and melts gradually to a liquid, which is clear at 83° (corr.).

o-*Methoxybenzylhexamethylenetetraminium chloride* has m. p., 201—202° (decomp.), the p-*isomeride*, m. p. 180—185° (decomp.).

2-*Methoxy*-1-*naphthylmethyl alcohol*, prepared by the addition of 2-methoxy-1-naphthylmethylamine to a mixture of 30% sodium nitrite solution and glacial acetic acid, forms colourless, glittering leaflets, m. p. 100—101° (corr.), and is converted by hydrogen chloride in benzene solution into the corresponding *chloride*, which yields a hexamethylenetetramine *compound*, m. p. 185—186° (decomp.).

5-*Nitro*-2-*methoxybenzyl alcohol*, obtained by the action of methyl-alcoholic sodium hydroxide on 5-nitro-2-methoxybenzaldehyde, crystallises in rosettes of long, straw-coloured needles, m. p. 124—125° (corr.), with preliminary softening; the *chloride* forms pale straw-coloured prisms, m. p. 80·5—81° (corr.), and yields a hexamethylenetetramine *compound*, m. p. 191—195° (decomp.).

3-Nitro-4-methoxybenzyl alcohol is readily prepared by the interaction of 3-nitroanisaldehyde and sodium hydroxide in cold methyl-alcoholic solution (compare Stoermer and Behn, A., 1901, i, 726), and when boiled with concentrated hydrochloric acid is converted into 3-*nitro*-4-*methoxybenzyl chloride*, which forms drab-coloured microcrystals, m. p. 86° (corr.), with preliminary sintering, and yields a hexamethylenetetramine *compound*, m. p. 183—188°, with darkening.

o-*Ethoxybenzylhexamethylenetetraminium chloride* crystallises in microscopic prisms and cubes, m. p. 188—191° (decomp.); 3 : 4-*methylenedioxybenzylhexamethylenetetraminium chloride*, from piperonyl chloride, has m. p. 203—204° (decomp.).

2 : 3-Dimethoxybenzyl chloride crystallises in needles, m. p. 69—70·5° with preliminary softening (compare Douetteau, A., 1912, i, 620); the hexamethylenetetramine *compound* forms rhombic crystals, m. p. 200—201° (decomp.).

2 : 4-*Dimethoxybenzyl alcohol*, prepared by heating 2 : 4-dimethoxybenzaldehyde with alcoholic potassium hydroxide, has b. p. 177—179°/10 mm.

3 : 4-*Dimethoxybenzylhexamethylenetetraminium chloride* separates from 95% alcohol in crystals, m. p. 159—165°, containing $1H_2O$; the anhydrous compound has m. p. 187—188° (decomp.) with preliminary softening and sintering.

2-*Nitro*-3 : 4-*dimethoxybenzylhexamethylenetetraminium chloride* crystallises in glistening leaflets, darkening at 175°, m. p. 187—189° (decomp.).

3-*Methoxy*-4-*ethoxybenzyl alcohol*, prepared by heating vanillin ethyl ether with alcoholic potassium hydroxide (compare Vavon, A., 1912, i, 260), is converted by hydrogen chloride in benzene solution at 0° into 3-*methoxy*-4-*ethoxybenzyl chloride*, which has b. p. 127°/0·6—0·7 mm., m. p. 42—42·5° with previous softening at 40°, and forms a hexamethylenetetramine *compound*, m. p. 178—181° (decomp.) with preliminary softening.

3-*Carboxy*-4-*hydroxybenzylhexamethylenetetraminium chloride*, from 5-chloromethylsalicylic acid, crystallises in irregular micro-plates, m. p. 188—190° (decomp.); the *methyl* ester, from methyl 5-chloromethylsalicylate, has m. p. 191—191·5° (decomp.).

3-*Carboxy*-2-*hydroxy*-5-*methylbenzylhexamethylenetetraminium chloride*, from chloromethyl-*p*-cresotic (2-hydroxy-3-chloromethyl-5-methylbenzoic) acid, forms a bright yellow powder, m. p. 179—181° (decomp.).

Methyl 3-*hydroxy*-4-*chloromethyl*-2-*naphthoate*, prepared from methyl 3-hydroxy-β-naphthoate (slightly yellow prisms, softening at 72°, m. p. 73·5—74° [corr.]) according to D.R.-P. 113723, separates from toluene in colourless, woolly masses of delicate needles, m. p. 164·5—166° (corr.) with preliminary softening, and yields a hexamethylenetetramine *compound*, $C_{19}H_{23}O_3N_4Cl$, which forms yellow micro-crystals, gives an indigo-blue coloration with ferric chloride, and when heated turns yellow, gradually softens, and decomposes at 195—198°.

5-*Carboxy*-2-*methoxybenzylhexamethylenetetraminium chloride*, from 4-methoxy-3-chloromethylbenzoic acid, has m. p. 204—205° (decomp.).

5-*Carbomethoxy*-2-*methoxybenzylhexamethylenetetraminium chloride*, from methyl 4-methoxy-3-chloromethyl benzoate, has m. p. 208—208·5° (decomp.).

4-*Hydroxy*-3-*aldehydobenzylhexamethylenetetraminium chloride*, from 5-chloromethylsalicylaldehyde, forms faintly yellow micro-crystals, decomposing at 194° after turning yellow.

2-*Hydroxy*-3-*methoxy*-5-*aldehydobenzylhexamethylenetetraminium*

chloride, from 4-hydroxy-5-methoxy-3-chloromethylbenzaldehyde, forms pale brown crystals, m. p. 163—164° (decomp.). F. B.

Quaternary Salts of Hexamethylenetetramine. II. Monohalogenacetylbenzylamides and their Hexamethylenetetraminium Salts. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Biol. Chem.*, 1915, **20**, 685—694. Compare preceding abstract).—The present paper deals with a number of chloroacetyl- and iodoacetylbenzylamides, and the quaternary salts obtained by their interaction with hexamethylenetetramine.

The halogenacetylbenzylamides were prepared from chloroacetohydroxymethylamide according to Einhorn's (A., 1906, i, 245; 1908, i, 608) method. In several instances the chloro-compounds reacted so unsatisfactorily with hexamethylenetetramine that it was found necessary to convert them into the iodides before good yields of the quaternary salts could be obtained.

Chloroacetobenzylamide, $CH_2Cl{\cdot}CO{\cdot}NH{\cdot}CH_2Ph$, prepared by the interaction of chloroacetyl chloride and benzylamine in the presence of aqueous potassium hydroxide at a low temperature, forms long, glistening hairs, m. p. 93·5—94·5° (corr.), with slight preliminary softening, and yields with hexamethylenetetramine an additive *compound*, $C_{15}H_{22}ON_5Cl$, microscopic rhombs, m. p. 168—169°, after darkening slightly.

Chloroaceto-o-methylbenzylamide, prepared in a similar manner, crystallises in long needles, m. p. 107·5—108° (corr.); the hexamethylenetetramine *compound* has m. p. 152°.

p-*Acetylamino*-N-*iodoacetylbenzylamine*, $C_{11}H_{13}O_2N_2I$, obtained by heating the corresponding chloroacetyl derivative (Einhorn and Mauermayer, *loc. cit.*) with sodium iodide in alcoholic solution, forms glistening needles, m. p. 205—206° (corr., decomp.) with preliminary darkening, and yields a hexamethylenetetramine *compound*, long, colourless needles, m. p. 165—166° (decomp.).

Chloroacetohydroxymethylamide condenses with aceto-*o*-toluidide in sulphuric acid solution, yielding 4-*acetylamino*-N-*chloroacetyl*-3-*methylbenzylamine*, $C_{12}H_{15}O_2N_2Cl$, which has m. p. 212·5—214° (corr.) with slight preliminary softening.

2-*Acetylamino*-N-*chloroacetyl*-5-*methylbenzylamine*, prepared from aceto-*p*-toluidide in a similar manner, melts incompletely at 164—167°, then resolidifies, and has m. p. 180—182°; the hexamethylenetetramine *compound* has m. p. 197—200°.

2-*Acetoxy*-N-*chloroacetyl*-α-*naphthylmethylamine*, obtained by warming the corresponding hydroxy-compound with acetic anhydride and a little sulphuric acid, crystallises in aggregates of long needles, m. p. 169—170° (corr.), and yields a hexamethylenetetramine *compound*, darkening at 170°, m. p. 175—176°; when heated with sodium iodide in acetone solution it is converted into 2-*acetoxy*-N-*iodoacetyl*-α-*naphthylmethylamine*, which crystallises in felted needles, sintering at 187°, m. p. 188—190° (corr.), and forms a hexamethylenetetramine *compound*, m. p. 184—187° (decomp.) with previous darkening at 175°.

5-*Nitro*-2-*acetoxy*-N-*chloroacetylbenzylamine*, prepared by acetylating

the corresponding hydroxy-compound, forms woolly masses of delicate, colourless needles, m. p. 97·5—98° (corr.) with preliminary softening.

The additive *compound* of 2-methoxy-*N*-chloroacetyl-α-naphthyl methylamine and hexamethylenetetramine separates from chloroform in crystals, m. p. 122·5—125° (decomp.), containing one molecule of the solvent; after removal of the chloroform by boiling with acetone it has m. p. 112—120°.

5-*Nitro*-2-*methoxy*-N-*chloroacetylbenzylamine*, prepared from the hydroxy-compound in the usual manner with methyl sulphate and aqueous potassium hydroxide, crystallises in faintly yellow, minute, glistening prisms, m. p. 120·5—121·5° (corr.) with softening at 113—114°.

The additive *compound* of 2-acetylamino-5-ethoxy-*N*-chloroacetylbenzylamine and hexamethylenetetramine has m. p. 169—170° (decomp.).

3 : 4-*Diacetoxy*-N-*chloroacetylbenzylamine*, prepared by acetylating the corresponding hydroxy-compound, forms sheaves of glistening, flat rods, m. p. 86·5—87·5° (corr.), and yields a hexamethylenetetramine *compound*, m. p. 174° (decomp.).

3 : 4-*Dimethoxy*-N-*chloroacetylbenzylamine*, obtained by the action of methyl sulphate and aqueous potassium hydroxide on the dihydroxy-derivative, crystallises in cream-coloured masses of delicate needles, m. p. 117—117·5° (corr.) with preliminary softening; the hexamethylenetetramine *compound* has m. p. 160—161° (decomp.).

Ethyl *N*-chloroacetyl-*m*-aminomethylbenzoate forms an additive *compound*, m. p. 122—124°, with hexamethylenetetramine, and reacts with sodium iodide in acetone solution, yielding *ethyl* N-*iodoacetyl*-m-*aminomethylbenzoate*, glistening, delicate needles, m. p. 116—116·5° (corr.) with preliminary softening.

N-*Chloroacetyl*-m-*aminomethylbenzoyl chloride*, prepared from the corresponding acid and phosphorus pentachloride in toluene solution, crystallises in aggregates of pale green prisms, m. p. 78—79° (corr.) with slight preliminary softening, and reacts with ammonia in chloroform solution and with diethylaminoethanol in pyridine solution, yielding the *amide*, m. p. 171—172·5° (corr.) with slight preliminary softening, and *β-diethylaminoethyl* ester, glistening platelets, sintering at 68°, m. p. 69—70·5°; the additive *compounds* of the amide and diethylaminoethyl ester with hexamethylenetetramine have m. p. 183° (decomp., with previous darkening at 175°) and 125—130° (with sintering at 120°) respectively. F. B.

Quaternary Salts of Hexamethylenetetramine. III. Monohalogenacylated Aromatic Amines and their Hexamethylenetetraminium Salts. Walter A. Jacobs and Michael Heidelberger (*J. Biol. Chem.*, 1915, **21**, 103—143).—In continuation of the work described in the preceding abstracts, the authors have prepared the chloroacetyl derivatives of a large number of aromatic amines and have examined the additive compounds which these derivatives form with hexamethylenetetramine. The additive compounds are readily soluble in water and undergo decomposition, particularly on boiling,

with the formation of methyleneglycyl derivatives of the original amines.

The chloroacetyl derivatives were all prepared by the gradual addition of a benzene solution of chloroacetyl chloride ($1\frac{1}{4}$ mols.) to the amines dissolved in toluene or benzene in the presence of excess of aqueous sodium hydroxide ($2N$), the mixture being well shaken and cooled.

When boiled with hexamethylenetetramine in chloroform solution, chloroacetanilide yields an additive *compound*, $C_{14}H_{20}ON_5Cl$, glistening micro-crystals, m. p. 158—159° (decomp.) with previous darkening at 155°; the additive *compound* with bromoacetanilide has m. p. 163° (decomp.); that with *N*-chloroacetylmethylaniline, m. p. 168—173° (decomp.), and separates with chloroform of crystallisation which may be removed by repeated extraction with boiling acetone. Chloroacetyldiphenylamine yields with hexamethylenetetramine the *compound* $C_{20}H_{24}ON_5Cl$; this crystallises with chloroform (1 mol) in hair-like needles (decomp. 158—161°), which after boiling with acetone contain two molecules of the latter solvent and then decompose at 151—162°. The *chloroacetyl* derivative of phenylglycineanilide separates with benzene of crystallisation and has m. p. 118—120° (corr.) with preliminary softening; the hexamethylenetetramine *compound* has m. p. 157—158°. N-*Chloroacetyl-ω-anilinoacetophenone*, almost colourless, hexagonal plates, m. p. 117—118° (corr.) with slight softening at 116·5°, forms a hexamethylenetetramine *compound*, m. p. 169—169·5° (decomp.). The additive *compound* of chloroaceto-*o*-toluidide with hexamethylenetetramine has m. p. 148—149° (decomp.).

N-*Bromoacetyl-ω-o-toluidinoacetophenone* crystallises in stout, diamond-shaped plates, m. p. 107—107·5°; the hexamethylenetetramine *compound* has m. p. 175—176° (decomp.). Chloroaceto-*m*-toluidide has m. p. 90—91·5° (corr.) and not 141° as given by Kuhara and Chikashigé (A., 1902, i, 227); the hexamethylenetetramine *compound* darkens above 170°, m. p. 173—174°.

The additive *compounds* with the following chloroacetyl derivatives are also described; chloroaceto-*p*-toluidide, m. p. 176—178° (decomp.); chloroaceto-*m*-4-xylidide, silky needles, m. p. 171—172°; chloroaceto ψ-cumidide, slender needles, m. p. 170—171° (decomp.); chloroaceto-*α*-naphthylamide, rosettes of needles, m. p. 164—166° (decomp.); chloroaceto-*β*-naphthylamide, m. p. 177—178° (decomp.).

Chloroaceto-*o*-chloroanilide, prepared from *o*-chloroaniline and chloroacetyl chloride in toluene solution, forms glistening needles, m. p. 73·5—74° (corr.) with previous softening at 71·5° (compare Schwalbe, Schulz and Jochheim, A., 1908, i, 974); the hexamethylenetetramine *compound* crystallises in glistening hairs, m. p. 158—160° (decomp.).

Chloroaceto-*p*-bromoanilide, prepared by brominating chloroacetanilide in glacial acetic acid solution (compare Frerichs, A., 1903, i, 610), forms a hexamethylenetetramine *compound*, $C_{14}H_{19}ON_5ClBr$, crystallising in prismatic needles with chloroform ($\frac{4}{5}$ mol.), half of which is retained even after drying over sulphuric acid under diminished pressure at the temperature of boiling alcohol.

Chloroaceto-2 : 4 : 6-*tribromoanilide*, obtained by heating chloroacetyl chloride with 2 : 4 : 6-tribromoaniline in toluene solution at 110—120°,

crystallises in needles, m. p. 221—222° (corr.), with partial decomposition.

Chloroaceto-m-*iodoanilide* forms slender, felted needles, m. p. 121·5—122·5° (corr.), and yields a hexamethylenetetramine *compound*, which becomes greenish at 170°, m. p. 175° (decomp.). *Chloroaceto*-5-*iodo*-o-*toluidide*, prepared from 5-iodo-o-toluidine, forms glistening needles, m. p. 161·5—162·5° (corr.) with slight preliminary softening; the hexamethylenetetramine *compound* crystallises in minute, flat prisms, m. p. 190—192° (decomp.).

The additive *compound* from chloroaceto-*m*-nitroanilide has m. p. 162—163°. Chloroaceto-*p*-nitroanilide forms pale yellowish-brown prisms, m. p. 182—184°, and not 152° as stated by Deutsch (A., 1907, i, 1082).

Chloroaceto-*m*-nitro-*p*-toluidide yields a pale yellow additive *compound*, m. p. 163—164° (decomp.).

Chloroaceto-m-*dimethylaminoanilide*, prepared from *m*-aminodimethylaniline, crystallises in greyish rhombs, m. p. 101·5—102·5° (corr.) with previous softening at 101°; the hexamethylenetetramine *compound* has m. p. 151—152° (decomp.).

p-Aminodimethylaniline is readily prepared by reducing *p*-nitrosodimethylaniline with stannous chloride and hydrochloric acid; the chloroacetyl derivative forms a hexamethylenetetramine *compound*, crystallising with chloroform in glistening plates, m. p. 145—148°, which, after drying under diminished pressure at the temperature of boiling alcohol, have the composition $C_{16}H_{25}ON_6,\frac{1}{2}CHCl_3$, and m. p. 171—172° (decomp.) with preliminary darkening.

p-*Aminodiethylaniline*, prepared from *p*-nitrosodiethylaniline in a similar manner, forms a pale yellow oil, b. p. 139·5—140·5°/9·5—10 mm.; the *chloroacetyl* derivative crystallises in faintly pink, lustrous needles, m. p. 83—84° (corr.), and yields a hexamethylenetetramine *compound*, glistening micro-crystals, m. p. 159—160° (decomp.).

p-*Nitrosodipropylaniline hydrochloride* is obtained as a greenish-yellow, microcrystalline powder by the addition of sodium nitrite to a cold solution of dipropylaniline in hydrochloric acid. It darkens and decomposes at about 160—165°, and on reduction with stannous chloride and hydrochloric acid is converted into p-*aminodipropylaniline*, which forms a viscid, pale yellow oil, b. p. 155·5—156·5°/6 mm., and yields a *chloroacetyl* derivative, almost colourless prisms, m. p. 121—121·5° (corr.) with previous softening at 120°. The last-mentioned compound forms with hexamethylenetetramine an additive *compound*, which crystallises with chloroform in minute platelets; after removal of the chloroform the compound has m. p. 165—168° (decomp.).

p-*Chloroacetylaminophenylbenzylethylamine*,

$$CH_2Cl\cdot CO\cdot NH\cdot C_6H_4\cdot NEt\cdot CH_2Ph,$$

prepared from *p*-aminophenylbenzylethylamine, crystallises in pale brownish micro-prisms, m. p. 106—108°, and yields a hexamethylenetetramine *compound* in glistening micro-platelets, m. p. 163—164° (decomp.).

p-*Chloroacetylaminoazobenzene*, $NPh{:}N\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2Cl$, forms sheaves of golden-yellow needles, m. p. 159·5° (corr.) with preliminary

softening at 155°; the orange-yellow additive *compound* with hexamethylenetetramine has m. p. 153—154° (decomp.).

5-o-*Tolueneazochloroaceto-o-toluidide*,

$$CH_2Cl\cdot CO\cdot NH\cdot C_6H_3Me\cdot N{:}N\cdot C_6H_4Me,$$

prepared from aminoazotoluene (from *o*-toluidine), crystallises in pale salmon-coloured needles, m. p. 171—172·5° (corr., decomp.) with previous softening at 168·5°, and yields an orange-yellow hexamethylenetetramine *compound*, m. p. 167—169°.

1 : *β*-Naphthaleneazo-2-naphthylamine forms a *chloroacetyl* derivative, bright orange, hair-like needles, m. p. 181·5—182·5° (corr.); the hexamethylenetetramine *compound* could not be obtained in a pure condition.

p-*Benzeneazobenzeneazochloroaceto-β-naphthylamide*,

$$NPh{:}N\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot NH\cdot CO\cdot CH_2Cl,$$

prepared from chloroacetyl chloride and 1-*p*-benzeneazobenzeneazo-2-naphthylamine, forms brick-red micro-needles, m. p. 190° (corr. decomp.) with previous darkening at 188°.

2′-4 : o-*Tolueneazo*-o-*tolueneazo*-1′-*naphthylamine*,

$$C_6H_4Me\cdot N_2\cdot C_6H_3Me\cdot N_2\cdot C_{10}H_6\cdot NH_2,$$

is obtained in glistening, dark violet-brown leaflets, m. p. 174—177°, by coupling diazotised aminoazotoluene (from *o*-toluidine) with *β*-naphthylamine in hydrochloric acid solution; the *chloroacetyl* derivative forms a brown, micro-crystalline powder, m. p. 122—126° (decomp.) with preliminary softening.

4-*o*-Tolueneazo-1-naphthylamine, m. p. 97—97·5° (corr.) (compare Casale and Casale-Sacchi, A., 1914, i, 1180), after diazotisation, couples with *β*-naphthylamine, yielding 4-o-*tolueneazo*-1 : 1′-*naphthaleneazo*-2′-*naphthylamine*, $C_6H_4Me\cdot N{:}N\cdot C_{10}H_6\cdot N{:}N\cdot C_{10}H_6\cdot NH_2$, which forms a blackish-brown, micro-crystalline powder, and gives an intense blue coloration with sulphuric acid.

4-Dimethylamino-4′-acetylaminoazobenzene has m. p. 226—227° (compare Meldola, T., 1884, **45**, 108), and is hydrolysed by hot dilute sulphuric acid to the free base, which reacts with chloroacetyl chloride, yielding 4-p-*dimethylaminobenzeneazochloroacetanilide*,

$$CH_2Cl\cdot CO\cdot NH\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot NMe_2,$$

glistening, chocolate-brown micro-plates, m. p. about 205° with previous sintering at 190°; the brown hexamethylenetetramine *compound* has m. p. 167—168·5°, gives orange solutions in water and purple in mineral acids.

4-*Acetylamino*-4′-*diethylaminoazobenzene*, prepared in the same manner as the dimethyl derivative, crystallises in glistening, orange-brown plates, softening at 186°, m. p. 192°, and is hydrolysed to 4-*amino*-4′-*diethylaminoazobenzene*, dark brown crystals, having a blue-black lustre, m. p. 149—150° (corr.) with preliminary softening; the *chloroacetyl* derivative forms chocolate-brown crystals, sintering at 155°, m. p. 160·5—162°, and yields a hexamethylenetetramine *compound*, m. p. 172—173° with previous sintering.

Diazotised *p*-aminoacetanilide couples with dipropylaniline, yielding 4-*acetylamino*-4′-*dipropylaminoazobenzene*, small, orange needles, m. p. 178° (corr.). This is transformed by hydrolysis and subsequent treatment with chloroacetyl chloride into 4-*chloroacetylamino*-4′-*dipropyl*-

aminoazobenzene, orange-brown micro-crystals, m. p. 112—114° (corr.) with preliminary softening and darkening, which yields a hexamethylenetetramine *compound*, orange-yellow micro-platelets, m. p. 180—181°, with previous sintering at 100°.

4-*Acetylamino*-4′-*benzylethylaminoazobenzene*,

$$CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NEt{\cdot}C_7H_7,$$

prepared by coupling diazotised *p*-aminoacetanilide with benzylethylaniline, crystallises from dilute alcohol with $\frac{1}{2}H_2O$ in minute brown rhombs with a violet reflex; the anhydrous substance has m. p. 148—150°. 4-*Chloroacetylamino*-4′-*benzylethylaminoazobenzene* has m. p. 140—141·5° (corr.), and yields a hexamethylenetetramine *compound*, ochreous micro-plates, sintering at 110°, m. p. 140° (decomp.).

m-*Bromodiethylaniline*, prepared by heating *m*-bromoaniline and ethyl iodide with sodium hydroxide and alcohol at 100°, is a highly refractive, colourless liquid, b. p. 139·5—142° (corr.)/9—10 mm., and couples with diazotised *p*-aminoacetanilide, yielding 2′-*bromo*-4-*acetylamino*-4′-*diethylaminoazobenzene*, minute, glistening rhombs, m. p. 163·5—164° (corr.) with previous sintering and reddening at 160°.

2-*Chloroacetylamino*-4′-*dimethylaminoazobenzene*, obtained by coupling benzenediazonium chloride with *m*-chloroacetylaminodimethylaniline, forms scarlet tablets, m. p. 109·5—110° (corr.) with slight preliminary softening.

4-*Nitro*-2′-*chloroacetylamino*-4′-*dimethylaminoazobenzene*, prepared from diazotised *p*-nitroaniline in a similar manner, separates from chloroform in dark violet-brown, voluminous, triboelectric masses of micro-crystals, m. p. 220°.

β-Naphthylamine couples with diazotised *p*-aminodiethylaniline, yielding 1-p-*diethylaminobenzeneazo*-2-*naphthylamine*, glistening, maroon plates, m. p. 117—120°, with preliminary softening.

4-p-*Diethylaminobenzeneazo*-1-*naphthylamine*, prepared from α-naphthylamine in a similar manner, could not be obtained in a crystalline condition; its *chloroacetyl* derivative forms chocolate-brown micro-crystals, which darken and soften at 120°, m. p. 145° (decomp.).

The additive *compound* of *o*-chloroacetylaminophenol and hexamethylenetetramine has m. p. 155° (decomp.), and gives a purple coloration with ferric chloride.

o-*Chloroacetylaminophenyl benzoate*, silky needles, has m. p. 107·5—108·5° (corr.); the hexamethylenetetramine *compound* is mentioned. o-*Chloroacetylaminophenyl* p-*nitrobenzoate* forms delicate interlaced needles, softening at about 160°, m. p. 163·5—164° (corr.), and yields a hexamethylenetetramine *compound*, pale yellow plates, which darken at 166°, m. p. 171—172°.

m-Aminophenol reacts with chloroacetic anhydride in boiling benzene solution, yielding m-*chloroacetylaminophenol*, colourless, glistening plates, m. p. 134·5—136° (corr.); the hexamethylenetetramine *compound* (decomp. 168° with preliminary darkening) crystallises with acetone ($\frac{1}{2}$ mol.).

3-*Chloroacetylamino*-4-*benzeneazophenol*, prepared by coupling *m*-chloroacetylaminophenol with diazotised aniline, forms minute, golden, inter-

laced needles, m. p. 200° (corr. decomp.), and yields a yellow hexamethylenetetramine *compound*, decomp. 202—230°.

p-*Chloroacetylaminophenyl chloroacetate*, obtained from chloroacetyl chloride and *p*-aminophenol in pyridine solution, crystallises in almost colourless spears, softening at 160°, m. p. 170—171° (corr.).

Chloroaceto-o-*anisidide*, flat needles, m. p. 48—48·5° (corr.), with slight preliminary softening, yields a hexamethylenetetramine *compound*, m. p. 151—153°. *α-Iodopropio*-o-*anisidide*, prepared from α-iodopropionyl chloride and *o*-anisidine in cold ethereal solution, crystallises in delicate needles, m. p. 95—96·5° (corr.), with slight preliminary softening. *β-Iodopropio*-o-*anisidide*, obtained from β-iodopropionyl chloride (b. p. 80·5—81·5°/15 mm.) in a similar manner, forms colourless, irregular plates, softening at 88°, m. p. 89—91° (corr.), and yields a hexamethylenetetramine *compound*, thin, glistening platelets, m. p. 172—173°.

N-*Chloroacetyl*-ω-o-*anisidinoacetophenone*,

$$CH_2Cl\cdot CO\cdot N(C_6H_4\cdot OMe)\cdot CH_2\cdot COPh,$$

forms prismatic needles, m. p. 101·5—102·5° (corr.); the hexamethylenetetramine *compound* crystallises in colourless micro-prisms, m. p. 145° (decomp.).

Chloroaceto-p-*anisidide*, glistening, transparent prisms, m. p. 121·5—122·5° (corr.) with previous softening, forms a hexamethylenetetramine *compound*, m. p. 164—167° (decomp.).

o-*Chloroacetylaminobenzyl alcohol*, prepared by the addition of chloroacetyl chloride to a well-cooled ethereal solution of *o*-aminobenzyl alcohol, crystallises in rosettes of needles, m. p. 103° (corr.); the hexamethylenetetramine *compound* is hygroscopic, and has m. p. 144—145° (decomp.).

o-*Chloroacetylaminobenzyl benzoate*, obtained by benzoylating the preceding alcohol in pyridine solution, forms snow-white needles, m. p. 113—113·5° (corr.) with slight preliminary softening, and yields a hexamethylenetetramine *compound*, darkening at 140°, m. p. 154—155° (decomp.).

The additive *compound* of ethyl *p*-chloroacetylaminobenzoate and hexamethylenetetramine has m. p. 155—156° (decomp.).

β-Diethylaminoethyl p-*chloroacetylaminobenzoate* (*chloroacetylnovocaine*), $CH_2Cl\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2\cdot NEt_2$, prepared from novocaine and chloroacetyl chloride, forms microscopic needles, m. p. 63—64·5° (corr.), and yields a hexamethylenetetramine *compound*, lenticular micro-platelets, which sinter at 126°, m. p. 128—129°.

m-*Chloroacetylaminoacetophenone* forms prisms, m. p. 113·5—114·5°; the hexamethylenetetramine *compound* crystallises in micro-platelets, m. p. 165—166° (decomp.), which are transformed into a mass of hair-like needles on treatment with alcohol.

4-*Chloroacetylamino*-4′ : 4″-*tetramethyldiaminotriphenylmethane*,

$$CH_2Cl\cdot CO\cdot NH\cdot C_6H_4\cdot CH(C_6H_4\cdot NMe_2)_2,$$

prepared from *p*-aminoleucomalachite green in the usual manner, forms pale greenish micro-crystals, which sinter above 80° and gradually soften to a tar when rapidly heated; the hexamethylenetetramine *compound* has m. p. 189—190° (decomp.).

2-*Chloroacetylamino*-4′ : 4″-*tetraethyldiaminotriphenylmethane* (not

isolated in a pure condition) yields a hexamethylenetetramine *compound*, colourless micro-platelets, m. p. 177—178° (decomp.). The hexamethylenetetramine *compound* of 4-*chloroacetylamino*-4′:4″-*tetraethyldiaminotriphenylmethane* forms micro-platelets, m. p. 168—169°.

6-*Chloroacetylaminoquinoline* crystallises in minute prisms, which become red, and have m. p. 153—155° (decomp.); the *hydrochloride* separates in pale, reddish-brown platelets, decomp. above 250° with previous darkening and sintering at 220°; the hexamethylenetetramine *compound* in pale drab-coloured micro-platelets, m. p. 203—204° (decomp.). F. B.

Quaternary Salts of Hexamethylenetetramine. IV. Monohalogenated Simple Amines, Carbamides, and Urethanes, and the Hexamethylenetetraminium Salts Derived Therefrom. Walter A. Jacobs and Michael Heidelberger (*J. Biol. Chem.*, 1915, **21**, 145—152. Compare preceding abstracts).—*α-Iodopropionamide*, prepared by the addition of the corresponding chloride to cold aqueous ammonia, crystallises in long, glistening needles, which soften and turn yellow above 150°, m. p. 159—160·5° (corr.). *β*-Iodopropionamide, obtained in a similar manner, forms feathery plates, m. p. 141·5—142·5 (corr.) with preliminary softening (Henry, A., 1885, 372, gives m. p. 100—101°); the additive *compound* with hexamethylenetetramine crystallises in broad, glistening needles, m. p. 169—170° (decomp.).

Chloroacetomethylamide, prepared by the addition of chloroacetyl chloride to a well cooled solution of methylamine in aqueous sodium hydroxide, forms delicate needles, m. p. 45—46° (corr.) with preliminary softening, and yields a hexamethylenetetramine *compound*, m. p. 173—174° (decomp.).

Chloroacetodimethylamide has b. p. 98·5—99·5° (corr.)/11 mm., m. p. 15·5° (corr.); the hexamethylenetetramine *compound*, m. p. 160—162°. *Chloroacetoethylamide*, b. p. 97·5—98·5°/13 mm., m. p. 22—22·5° (corr.), yields a hexamethylenetetramine *compound*, stout, hexagonal plates, m. p. 167—168° (decomp.) with previous darkening at 160°. *Chloroacetodiethylamide* is a highly refractive liquid, b. p. 126·5—128·5°/21 mm.; the hexamethylenetetramine *compound* crystallises in glistening rhombs, melting at 174° to a turbid liquid, which, on further heating, becomes clear, darkens, and finally effervesces above 190°.

The hexamethylenetetramine *compound* of *chloroacetopiperidide* [a viscid, almost colourless liquid, b. p. 143·5—145·5°/12·5 mm. (corr.)], forms micro-platelets; it becomes pasty at 168—170°, m. p. 184° (decomp.).

Methylenebisiodoacetamide, $CH_2(NH{\cdot}CO{\cdot}CH_2I)_2$, prepared by heating the corresponding chloro-compound (Einhorn and Mauermeyer, A., 1906, i, 250) with sodium iodide in acetone solution, crystallises in arborescent masses of thin plates, which darken above 220° when rapidly heated, and decompose at 227—229° with evolution of iodine; the hexamethylenetetramine *compound* could not be isolated in a pure condition.

Ethylenebischloroacetamide (N : N′-*dichloroacetylethylenediamine*) is obtained in prismatic needles, m. p. 174—176° (corr.) with preliminary

softening, by the interaction of chloroacetyl chloride and ethylenediamine hydrochloride in the presence of aqueous sodium hydroxide.

The additive *compound*, $C_9H_{17}O_2N_6Cl$, of chloroacetylcarbamide and hexamethylenetetramine crystallises in plates, m. p. 176—177° (decomp.), when freshly prepared, but when kept for several weeks has m. p. 191—192°; the *compound*, $C_{10}H_{19}O_2NCl$, from chloroacetylmethylcarbamide forms long needles, which sinter at 149—151° and gradually melt, decomposing at 178°.

Chloroacetyl chloride reacts with benzylcarbamide in boiling benzene solution, yielding *N-chloroacetylbenzylcarbamide*, $C_{10}H_{11}O_2N_2Cl$, glistening needles, m. p. 153—155° (corr.), which forms a hexamethylenetetramine *compound*, long, silky needles, m. p. 160°.

The additive *compound*, $C_{11}H_{20}O_3N_5Cl$, of chloroacetylurethane and hexamethylenetetramine has m. p. 166—167°. F. B.

Preparation of Aniline-*o*-sulphonic Acid. J. Obermiller (D.R.-P. 281176; from *J. Soc. Chem. Ind.*, 1915, **34**, 543).—The product of the sulphonation of benzene, containing as little sulphuric acid as possible, is nitrated at a temperature above the normal, the mixture of nitro-acids is reduced, and the anilinesulphonic acids are separated by fractional crystallisation of the magnesium salts. As an alternative, the nitrobenzenesulphonic acids are separated in the same way, before reduction. The salts of the ortho-acids are the most soluble (compare A., 1914, i, 513). J. C. W.

Preparation of Monohydric Phenols and their Monochloro-substitution Products. Chemische Werke Ichendorf (D.R.-P. 281175; from *J. Soc. Chem. Ind.*, 1915, **34**, 543).—The mono- or di-chloro-derivatives of aromatic hydrocarbons are heated with an alkali hydroxide and methyl alcohol for a long time. The method gives good yields in the preparation of phenol from chlorobenzene, *o*- or *p*-chlorophenol from *o*- or *p*-dichlorobenzene, or α-naphthol from α-chloronaphthalene (compare Meyer and Bergius, this vol., i, 231). J. C. W.

Action of Formaldehyde on Phenols in the Presence of Concentrated Sulphuric Acid. J. Buraczewski (*Chem. Zentr.*, 1914, ii, 1267).—When phenol dissolved in concentrated sulphuric acid is shaken with a cold, freshly prepared solution of 40% aqueous formaldehyde in concentrated sulphuric acid, the mass suddenly solidifies. The solid product is green, but paler in colour according to the cooling of the mixture; it is insoluble in organic solvents. The colour changes to pale yellow under the action of alkalis, and in this respect ammonia or potassium cyanide is more active than sodium or potassium hydroxide. If the solution of phenol in sulphuric acid is warmed and then cooled previous to the addition of formaldehyde, a solid product is not formed. When however, hot solutions of the components are mixed, solidification takes place, and an intensely green mass results; at a higher temperature a black product is obtained. The compounds have an antiseptic and deodorising action; after treatment with a small quantity of these products, fresh urine showed no sign of decomposition after a long period. H. W.

Dihydroresorcinols [*cyclo*Hexane-1 : 3-diones] and their Reduction. A. E. USPENSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 738—751).—The author has investigated the reduction, by means of sodium and alcohol, of *cyclo*hexane-3 : 5-dione and its 1-methyl-, 1 : 1-dimethyl-, 1 : 1 : 2-trimethyl-, and 1-phenyl-derivatives into the corresponding *cyclo*hexane-3 : 5-diols (compare Crossley, T., 1901, **79**, 138; Crossley and Renouf, T., 1911, **99**, 1101).

1 : 1-Dimethyl*cyclo*hexane-3 : 5-diol has m. p. 145—146° (compare Zelinski and Uspenski, A., 1913, i, 607). 1 : 1 : 2-*Trimethyl*cyclo*hexane*-3 : 5-*diol*, $C_9H_{18}O_2$, forms a lustrous, white, microcrystalline powder, m. p. 149°, with a bitter-sweet taste. 1-*Phenyl*cyclo*hexane*-3 : 5-*diol*, $C_{12}H_{16}O_2$, forms crystals, m. p. 160°, with a bitter-sweet taste. cyclo*Hexane*-1 : 3-*diol*, obtained as a liquid, b. p. 138—141°/11 mm. (compare Sabatier and Mailhe, A., 1908, i, 529), gives an *acetyl* derivative, b. p. 127—128°/11 mm.

The maximum yield of reduction product is obtained with 1 : 1-dimethyl*cyclo*hexane-3 : 5-dione, and the minimum with the non-substituted diketone and its 1 : 1 : 2-trimethyl derivative, the 1-phenyl compound occupying an intermediate position. Just as was found for the dissociation constants (compare Schilling and Vorländer, A., 1899, i, 878), no relation appears to exist between the capacity of these compounds to undergo reduction and the accumulation of methyl groups in the molecule. Further, no relation is apparent between the reduction of these compounds and their hydrolysis by means of alkali. Thus, 1 : 1-dimethyl*cyclo*hexane-3 : 5-dione is hydrolysed with difficulty, but reduced readily, whilst *cyclo*hexane-1 : 3-dione and 1-phenyl*cyclo*hexane-3 : 5-dione are hydrolysed with ease, but give poor yields of reduction product; 1 : 1 : 2-trimethyl*cyclo*hexane-3 : 5-dione is difficult either to hydrolyse or to reduce. T. H. P.

Inositol and Pinitol and Some of their Derivatives. EDWARD G. GRIFFIN and J. M. NELSON (*J. Amer. Chem. Soc.*, 1915, **37**, 1552—1571).—This investigation was undertaken with the object of effecting the synthesis of inositol or of compounds closely related to it. This aim was not achieved, but various derivatives of inositol were obtained and characterised.

Inositol hexa-acetate (hexa-acetoxy*cyclo*hexane) can be readily obtained by treating inositol with acetyl bromide. If the reaction is carried out in a sealed tube at 120°, however, this substance is not produced, but a mixture of the following compounds is obtained: Penta-acetoxy*cyclo*hexyl bromide, m. p. 240°; α- and β-dibromotetra-acetoxy*cyclo*hexanes, m. p. 225° and 130°; *dibromotriacetoxy*cyclo*hexanol*, $C_6H_6Br_2(OAc)_3{\cdot}OH$, m. p. 124°, slender prisms, and *dibromodiacetoxy*cyclo*hexanediol*, $C_6H_6Br_2(OAc)_2(OH)_2$, m. p. 214° (decomp.), soft, white needles, which on acetylation yields β-dibromotetra-acetoxy*cyclo*hexane; *tribromotriacetoxy*cyclo*hexane*, $C_6H_6Br_3(OAc)_3$, m. p. 180°, microscopic plates; and dibromo*cyclo*hexanetetra-ol, m. p. 216° (decomp.). The first three and the last of these compounds have been described by Müller (T., 1907, **91**, 1780).

When inositol is heated with acetyl chloride in a sealed tube at 140°, the following substances are produced. *Chloropenta-acetoxy-*

cyclohexane, $C_6H_6Cl(OAc)_5$, m. p. 250°, slender crystals; *α-dichlorotetra-acetoxycyclohexane*, $C_6H_6Cl_2(OAc)_4$, m. p. 186°, lustrous scales; *β-dichlorotetra-acetoxycyclohexane*, m. p. 118°, brilliant, rhombic prisms; *dichlorotriacetoxycyclohexanol*, $C_6H_6Cl_2(OAc)_3{\cdot}OH$, b. p. 216—217°/2·3 mm., amorphous, which on acetylation yields β-dichlorotetra-acetoxy*cyclo*hexane, and *dichlorocyclohexanetetra-ol*, $C_6H_6Cl_2(OH)_4$, m. p. 221°, small prisms.

When heated with benzoyl chloride and quinoline at 120°, inositol yields hexabenzoyloxy*cyclo*hexane, m. p. 258°; *pentabenzoyloxycyclohexanol*, $C_6H_6(OBz)_5{\cdot}OH$, m. p. 269°, transparent prisms; and *tetrabenzoyloxycyclohexanediol*, $C_6H_6(OH)_2(OBz)_4$, m. p. 231°, a white, amorphous powder.

By the action of anisoyl chloride and quinoline on inositol, the *hexa-* and *penta-anisoyl* derivatives, m. p. 225° and 251°, are obtained, which crystallise in slender prisms and microscopic needles respectively.

When inositol is heated with cinnamoyl chloride and quinoline, the following derivatives are produced. The *hexacinnamoyl* derivative, m. p. 199°, slender needles; the *α-pentacinnamoyl* derivative, m. p. 271°, microscopic prisms; and the *β-pentacinnamoyl* derivative, m. p. 125°, a white, amorphous powder.

m-Nitrobenzoyl chloride and quinoline similarly react with inositol with formation of the *penta*-m-*nitrobenzoyl* derivative, m. p. 226°, a white powder, and the *hexa*-m-*nitrobenzoyl* derivative, m. p. 217°, slender needles.

By the action of ethyl chlorocarbonate on inositol in presence of quinoline, a syrupy product is obtained which probably contains inositol carbonates, and on acetylation yields two isomeric hexa-acetyl derivatives which are both different from that obtained by the direct acetylation of inositol. *α-Hexa-acetoxycyclohexane*, m. p. 212°, forms small, flat prisms, and the *β-compound*, m. p. 200°, microscopic prisms.

The following ethers were obtained by the methylation of inositol and the acetylation of the products. *Methoxycyclohexanepenta-ol*, $OMe{\cdot}C_6H_6(OH)_5$, m. p. 204°, microscopic prisms; *penta-acetoxymethoxycyclohexane*, $OMe{\cdot}C_6H_6(OAc)_5$, m. p. 141°, long, white needles; *tetra-acetoxydimethoxycyclohexane*, $C_6H_6(OMe)_2(OAc)_4$, m. p. 223°, which forms small prisms and sublimes above 300°; *triacetoxydimethoxycyclohexanol*, $C_6H_6(OMe)_2(OAc)_3{\cdot}OH$, b. p. 212—213°/2·5 mm., a syrupy liquid.

The following ethyl ethers were prepared in a similar manner. *Penta-acetoxyethoxycyclohexane*, $OEt{\cdot}C_6H_6(OAc)_5$, m. p. 128°, long, white needles; *tetra-acetoxydiethoxycyclohexane*, $C_6H_6(OEt)_2(OAc)_4$, m. p. 212°, which forms small prisms and sublimes above 300°; and *diethoxycyclohexanetetra-ol*, $C_6H_6(OEt)_2(OH)_4$, m. p. 212°, small, lustrous prisms.

By the acylation of pinitol, the following compounds were obtained. *Penta-acetoxymethoxycyclohexane*, $OMe{\cdot}C_6H_6(OAc)_5$, m. p. 98°, $[\alpha]_D^{20} - 9{\cdot}67°$, slender prisms; *pentabenzoyloxymethoxycyclohexane*, m. p. 97°, $[\alpha]_D^{20} + 32{\cdot}3°$, a white, amorphous powder; *penta-anisoyloxymethoxycyclohexane*, m. p. 101°, long, white needles; and *penta-*

cinnamoyloxymethoxycyclohexane, m. p. 105°, $[\alpha]_D^{20}$ +41·2°, a white, amorphous powder.

When pinitol is heated with acetyl bromide in a sealed tube, α- and β-dibromotetra-acetoxy*cyclo*hexanes are produced. E. G.

Preparation of Derivatives of *p*-Acylaminophenyl Alkyl Ethers. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 280225).—Derivatives of the type NRAcyl·C_6H_4·OR′, in which R = H, alkyl, acyl, aryl or arylalkyl and R′ = hydroxyalkyl, have particular medical interest, for they are much less antipyretic than analgesic, and do not lead to the formation of hæmoglobin like phenacetin. They are prepared by treating *p*-acylaminophenols with polyhydric alcohols or their anhydrides or halogen hydrins or by acylating the *p*-aminophenyl hydroxyalkyl ethers.

For example, *p*-acetylaminophenol is boiled with aqueous-alcoholic potassium hydroxide and treated with α-monochlorohydrin, when p-*acetylaminophenyl glycerol ether*,

$$NHAc\cdot C_6H_4\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH,$$

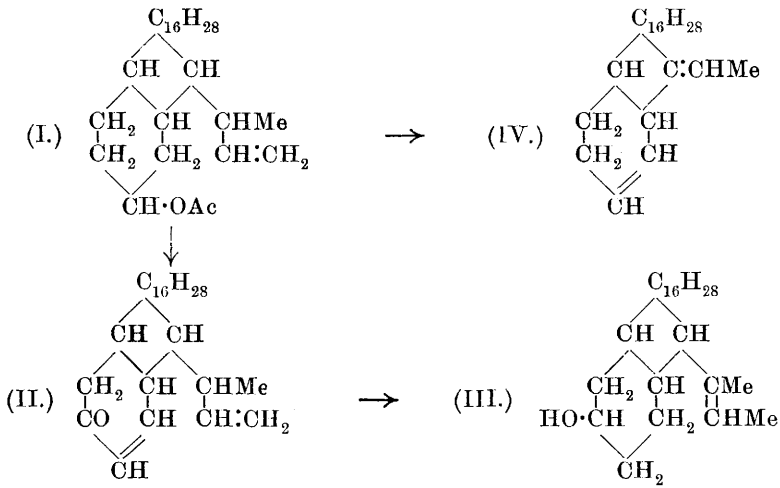
is obtained by evaporating the filtrate, in colourless crystals, m. p. 138°. The same ether is also prepared by heating *p*-acetylaminophenol, glycerol, and anhydrous sodium acetate for fifteen hours at 200—210°. Glycol chlorohydrin gives p-*acetylaminophenyl glycol ether*, $NHAc\cdot C_6H_4\cdot O\cdot CH_2\cdot CH_2\cdot OH$, m. p. 120°, which is also the product when *p*-acetylaminophenol and ethylene oxide are heated at 150° for ten hours in a sealed tube. This ether forms a *urethane*, m. p. 104°, when treated with ethyl chloroformate and pyridine in solution in much acetone. p-2 : 4-*Dinitroanilinophenyl glycol ether*, m. p. 128°, is acetylated by glacial acetic acid at 70°, and the p-2 : 4-*dinitroacetanilinophenyl glycol ether*, $C_6H_3(NO_2)_2\cdot NAc\cdot C_6H_4\cdot O\cdot CH_2\cdot CH_2\cdot OH$, forms reddish-brown crystals, m. p. 113°. J. C. W.

Cholesterol. XX. Oxidation of Cholesteryl Acetate with Chromic Acid. A. WINDAUS and C. RESAU (*Ber.*, 1915, **48**, 851—857).—Mauthner and Suida (A., 1897, i, 31) obtained as the chief product of the oxidation of cholesteryl acetate (I) by chromic acid, β-oxycholestenyl acetate. This ester was hydrolysed to the ketonic alcohol, which readily changed into an unsaturated ketone, oxycholesterylene (II). The authors have re-opened this subject. They find that the latter compound is apparently doubly unsaturated. By the prolonged action of hydrogen in the presence of spongy platinum, it is converted into β-cholestane, which shows that it contains the same carbon skeleton as cholesterol. When boiled with sodium and alcohol, it changes into an isomeride of cholesterol, designated *ψ-cholesterol* (III), which crystallises in colourless needles, m. p. 116°, and forms a *benzoate*, m. p. 155—156°. It differs from cholesterol in that it has $[\alpha]_D^{20}$ +57·59°, and does not form additive compounds with saponins. When the hydroxyl group is replaced by hydrogen (by the action of phosphorus pentachloride, followed by reduction with sodium and alcohol) it yields ψ-cholestene (Mauthner, A., 1907, i, 921).

It is also found that acidic compounds accompany the β-oxy-

cholestenyl acetate. These were isolated as very viscous substances which seemed to contain the acetate of a hydroxy-acid. When distilled from a bath at 320°, under 25 mm., the product yielded a *hydrocarbon*, $C_{25}H_{40}$ (IV), in needles, m. p. 76°, $[\alpha]_D^{20} - 142{\cdot}9°$, which formed a *dibromide*, long, thin needles, m. p. 147°. It really contained two ethylene linkings, for catalytic reduction led to a mixture of isomeric *hydrocarbons*, $C_{25}H_{44}$, which were separated by repeated crystallisation from alcohol. The less soluble isomeride formed long, thin needles, m. p. 80°, the other, thin leaflets, m. p. 55—59°. They were freed from any residual unsaturated hydrocarbon by adding acetic anhydride and concentrated sulphuric acid to a solution of the crude product in ether. On evaporation of the solvent, the saturated hydrocarbons crystallised, leaving the unsaturated compound in solution as a substance which dissolved in water. This process for purifying a saturated hydrocarbon is of general application (see following abstract).

The relationships of the more important of these derivatives to cholesteryl acetate (I) are given by the following scheme.

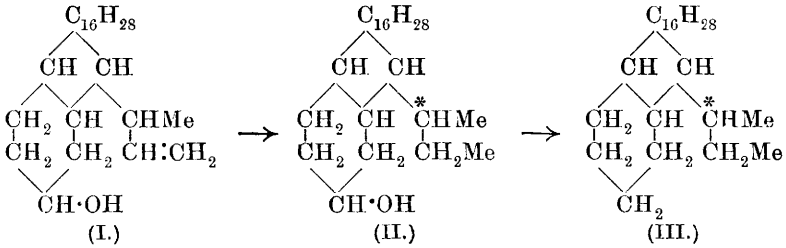


J. C. W.

Cholesterol. XXI. Coprosterol. A. Windaus and Cl. Uibrig (*Ber.*, 1915, **48**, 857—863).—A continuation of the work on reduced cholesterols (compare A., 1914, i, 1066).

A. It has been shown that coprosterol is different from β-cholestanol, the normal reduction product of cholesterol, and also that the corresponding ketones are not identical (Dorée and Gardner, T., 1908, **93**, 1630). It is now shown that the corresponding saturated hydrocarbons, β-cholestane and *coprostane*, are also different substances. The latter was prepared by converting coprosterol into the chloride, reducing this by sodium and amyl alcohol, and purifying the product by the process described above (preceding abstract). It is found to be identical, however,

with ψ-cholestane. Mauthner demonstrated the connexion between β-cholestane and ψ-cholestane in the following way (A., 1909, i, 714). The hydroxyl group of cholesterol (I) was replaced by hydrogen, yielding cholestene, which gave β-cholestane by catalytic reduction and ψ-cholestane by the addition and subsequent elimination of hydrogen chloride. These hydrocarbons (III) are therefore supposed to differ in the arrangement of a methyl group and a hydrogen atom about an asymmetric carbon atom, *, and coprosterol and β-cholestanol (II) are isomeric in the same sense.



B. When coprosterol is boiled with sodium and amyl alcohol, about 90% is converted into the isomeride, ψ-coprosterol, which differs merely in the arrangement of the hydroxyl group in space (compare Dorée and Gardner, *loc. cit.*). As in the similar case of β-cholestanol and its isomeride, ε-cholestanol (*loc. cit.*), the pseudo-form does not combine with digitonin. A fact which is of importance in the theoretical considerations is that this ψ-coprosterol, m. p. 117°, when mixed with an equimolecular quantity of β-cholestanol, m. p. 142°, in hot, concentrated solution in light petroleum, forms a *partial racemate*, which quickly separates in long needles, m. p. 152°. This double compound is also formed when cholesterol is reduced by means of nickel and hydrogen at 200° (future communication). Although β-cholestanol crystallises with $1H_2O$, the double compound is free from water of crystallisation. The components are separated by digitonin, which precipitates the β-cholestanol.

C. The recorded m.p.'s of coprosterol derived from fæces vary considerably, whereas a specimen obtained by the action of sodium and amyl alcohol on the above ψ-coprosterol (the reversion only takes place to a slight extent) has m. p. 104—105°. A sample, m. p. 112—116°, supplied by Fischer (A., 1911, i, 803) has now been found to contain a little β-cholestanol. Böhm had also found β-cholestanol in a closed intestine several years after an operation (A., 1911, ii, 274).

J. C. W.

The Double Bonds of the Cholesterol Molecule. Otto von Fürth and Gustav Felsenreich (*Biochem. Zeitsch.*, 1915, **69**, 416—444). —The addition of hydrogen in the presence of platinum by the method of Willstätter and Hatt was investigated quantitatively in a shaking apparatus, which is fully described and figured in the text. It was found that cholesterol and cholestene, when converted into cholestane, absorb the amount almost exactly equivalent to two atoms per molecule of substance reduced. Dihydrocholesterol absorbs two atoms

of bromine, almost exactly the same amount as is absorbed by cholesterol; the addition follows, however, much more slowly in the former case, and no bromine additive product could be isolated. A chemical compound which is easily dissociated or a physico-chemical complex appears therefore to be formed. Cholesterol absorbs 1·5—4 molecules of ozone, dihydrocholesterol 1·8—4·3 molecules, cholestane 1·5—4·8 molecules. This addition appears to lead to the formation of secondary (oxidation?) products, and the ozone numbers cannot be regarded as chemical constants. The general results of the investigations lead to the conclusion that there is no double bond in the cholesterol molecule other than that of the vinyl group. S. B. S.

Phthalylidenephenyl*iso*crotonic Acid. W. Borsche and G. Heimbürger (*Ber.*, 1915, **48**, 966—972).—Sodium γ-phenyl*iso*crotonate undergoes condensation with benzaldehyde in the presence of acetic anhydride at 100°, giving phenylbenzylidene*iso*crotonic acid and diphenylbutadiene. Under similar conditions, condensation can be effected with phthalic anhydride, the product being *α-phthalylidene-γ-phenylisocrotonic acid*, $CO<_{-O-}^{C_6H_4}>C{:}C(CO_2H)\cdot CH{:}CHPh$, yellow needles, m. p. 252°, which is generally accompanied by a little phthalylidenestyrylmethane. The former substance can alternatively be regarded as the lactone of the enolic form of *α-o*-carboxybenzoyl-*α*-styrylacetic acid; it dissolves in sodium carbonate solution, but if the solution is boiled, acidification causes the separation, not of the original substance, but of *ω-styrylacetophenone-o-carboxylic acid*,

$$CO_2H\cdot C_6H_4\cdot CO\cdot CH_2\cdot CH{:}CHPh,$$

a yellow, amorphous solid, which when heated with a mixture of acetic and hydrochloric acids or with alcoholic sulphuric acid undergoes intramolecular condensation to *cinnamylidenephthalide*,

$$CO<_{-O-}^{C_6H_4}>C{:}CH\cdot CH{:}CHPh,$$

a yellow, crystalline solid, m. p. 144—145°. This substance, however, is more conveniently obtained by heating phthalylidenephenyl*iso*crotonic acid at 270°, or especially by boiling with alcoholic sulphuric acid; it forms a *dibromide*, colourless needles, m. p. 159—160° (decomp.), and condenses with hydrazine in diluted acetic acid solution, forming pale yellow needles of the *phthalazone*,

$$CO<_{NH\cdot N}^{-C_6H_4-}>C\cdot CH_2\cdot CH{:}CHPh,$$

m. p. 201°, which is also produced by the action of the same reagent on phthalylidenephenyl*iso*crotonic acid, although in alcoholic solution the product from the last named is phthalylhydrazide, due to intermediate molecular fission.

Attempts to produce the methyl or ethyl ester of the unstable ω-styrylacetophenone-*o*-carboxylic acid by the action of sodium methoxide or ethoxide on cinnamylidenephthalide, which may be regarded as the corresponding lactone, yielded, after acidification, 1 : 3-*diketo*-2-*styrylhydrindene*, $C_6H_4<_{CO}^{CO}>CH\cdot CH{:}CHPh$, needles,

m. p. 162°; this gives crystalline condensation products with hydroxylamine and phenylcarbamic hydrazide.

For the purpose of comparison, *α-phthalidyl-γ-phenylbutyric acid*, $CO<^{C_6H_4}_{---O---}>CH\cdot CH(CO_2H)\cdot CH_2\cdot CH_2Ph$, was prepared by the reduction of phthalylidenephenyl*iso*crotonic acid with hydrogen and colloidal palladium. This substance is a yellow, viscid liquid; the *ethyl* ester, silky needles, has m. p. 68—69°. D. F. T.

Preparation of Acid Ferrous Salts of Aromatic Hydroxycarboxylic Acids and their Derivatives. M. Claass (D.R.-P. 279865; from *J. Soc. Chem. Ind.*, 1915, **34**, 451).—Hot aqueous solutions of the alkali salts of hydroxybenzoic acids or their homologues, or substitution products, are treated with ferrous sulphate and a small amount of a reducing agent, such as sodium hyposulphite. The acid ferrous salt, for example, the salicylate, crystallises on cooling. The salts may be used as antiseptics. J. C. W.

Preparation of Calcium *o*-Acetoxybenzoate. Soc. Chim. Usines du Rhône, Anct. Gillard, P. Monnet et Cartier (D.R.-P. 275038).—Calcium *o*-acetoxybenzoate separates quantitatively, in very slender needles, when an anhydrous solution of *o*-acetoxybenzoic acid and calcium chloride in methyl or ethyl alcohol is treated with gaseous or alcoholic ammonia. J. C. W.

Some Reactions of Calcium Salicylate. W. Œchsner de Coninck (*Rev. gen. Chim. pure appl.*, 1914, **17**, 201).—Salicylic acid is displaced from calcium salicylate by sulphurous acid, sodium hydrogen sulphite, potassium hydrogen sulphate, ordinary alum, chrome alum, iron ammonium alum, potassium hydrogen acetate and potassium hydrogen propionate. The following substances are without action on calcium salicylate: potassium ferro- and ferri-cyanides, potassium dichromate, potassium trichromate, chromic acid, sodium thiosulphate, and methyl-, ethyl- and amyl-sulphuric acids. Calcium salicylate differs from calcium *p*-hydroxybenzoate in that it does not set solid with water and does not combine with methyl alcohol. W. G.

Preparation of Methyl Menthylsalicylate. G. Blieberger (U.S. Pat. 1133832; from *J. Soc. Chem. Ind.*, 1915, **34**, 575).—Methyl salicylate (100 parts) is heated with menthol (80 parts) in an inert atmosphere under slight pressure. After removing the first distillate, the remainder is distilled in a vacuum. J. C. W.

Derivatives of *o*-Acetoxybenzoic Acid Compounds. Synthetic Patents Co., New York (U.S.Pat. 1122201; from *J. Soc. Chem. Ind.*, 1915, **34**, 451).—Antipyretic and antineuralgic compounds of the type $RO\cdot CO\cdot R'\cdot O\cdot CO\cdot R''$, where R = the residue of salicylic acid or one of its derivatives, R′ = an alkyl radicle, and R″ = any organic radicle, are described. For example, acetylglycolyl chloride and salicylic acid are condensed in the presence of dimethylaniline diluted with benzene, forming *o-acetylglycolyloxybenzoic acid*,

$$CO_2H\cdot C_6H_4\cdot O\cdot CO\cdot CH_2\cdot OAc,$$

m. p. 103°. Similar compounds include *acetylglycolyloxy*-m-*toluic acid*, m. p. 108°, *acetylglycolyloxy*-p-*toluic acid*, m. p. 151°, *chloro*-o-*acetylglycolyloxybenzoic acid*, m. p. 135°, *iodo*-o-*acetylglycolyloxybenzoic acid*, m. p. 144°, *oxyacetyl-lactyl*-p-*toluic acid*, m. p. 128°, o-*cinnamoylglycolyloxybenzoic acid*, m. p. 135°, and o-*anisoylglycolyloxybenzoic acid*, m. p. 123°. J. C. W.

Preparation of Protocatechuic Acid and Protocatechualdehyde. Ludwig Schmidt (D.R.-P. 278778).—For the preparation of protocatechuic acid, piperonaldehyde is treated with chlorine (3 mol.) in carbon tetrachloride, and when the colour has disappeared, the solvent is evaporated and the residue is decomposed by water and finally boiled, when the pure acid separates in quantitative yield, on cooling. The reactions are represented by the equations:

$$CH_2O_2{:}C_6H_3{\cdot}CHO + 3Cl_2 \longrightarrow CCl_2O_2{:}C_6H_3{\cdot}COCl;$$

this $+ 3H_2O \longrightarrow C_6H_3(OH)_2{\cdot}CO_2H$.

When the aldehyde is first converted into piperonylidene dichloride by the action of phosphorus pentachloride (or phosphorus and chlorine) in toluene, then treated with 2 mols. of chlorine and finally decomposed by water, a quantitative yield of protocatechualdehyde is obtained; thus:

$$CH_2O_2{:}C_6H_3{\cdot}CHO + PCl_5 + 2Cl_2 \longrightarrow CCl_2O_2{:}C_6H_3{\cdot}CHCl_2;$$

this $+ 3H_2O \longrightarrow C_6H_3(OH)_2{\cdot}CHO$. J. C. W.

Preparation of Alkyl Esters of Triacetylgallic Acid. Farbenfabriken vorm. F. Bayer & Co. (D.R.-P. 279958; from *J. Soc. Chem. Ind.*, 1915, **34**, 452).—The alkyl esters of gallic acid (except the methyl ester) are acetylated, or triacetylgallic acid is converted into the alkyl esters (except the methyl ester) by the usual methods. The products have astringent properties. J. C. W.

Determination of the Configuration of Stereoisomeric Stilbenes and of their Carboxylic Acids. R. Stoermer (*Annalen*, 1915, **409**, 13—19).—When the stable 2-nitro-α-phenylcinnamic acid, m. p. 196°, is reduced and the product diazotised, phenanthrene-9-carboxylic acid is obtained with great ease, whilst the labile 2-nitro-α-phenylcinnamic acid, after the same treatment, does not yield a trace of the phenanthrenecarboxylic acid. Consequently, the stable acid has the *cis*-configuration (I) and the labile acid the *trans*-configuration (II):

(I.) $NO_2{\cdot}C_6H_4{\cdot}CH$ (II.) $NO_2{\cdot}C_6H_4{\cdot}CH$

$PhC{\cdot}CO_2H$ $CO_2H{\cdot}CPh$

These conclusions are confirmed as follows. The amino-acid obtained by the reduction of the labile acid can only exist in the form of its salts. When the acid is liberated, it changes quantitatively to 3-phenylcarbostyril; moreover, when a solution of the barium salt is diazotised and boiled, 3-phenylcoumarin is obtained quite smoothly. Consequently, in the labile 2-nitro-α-phenylcinnamic acid the nitrophenyl and the carboxyl groups must be in the *cis*-position with respect to one another.

The replacement of the amino-group by hydrogen in the two 2-amino-α-phenylcinnamic acids presents very great difficulties. No method has

been successful in the case of the *cis*-acid, the product always being phenanthrene-9-carboxylic acid. In the case of the *trans*-(*allo*-)acid, the only successful method is to add slowly a diazotised solution to a hot saturated solution of sodium hypophosphite containing copper bronze as a catalyst; the product, which is obtained in good yield, is *allo*-α-phenylcinnamic acid, m. p. 137°, which has, therefore, the *trans*-configuration. By exclusion, the stable α-phenylcinnamic acid, m. p. 172°, has the *cis*-configuration.

When the α-phenylcinnamic acids are heated with barium oxide at about 300°/12—13 mm., the stable (*cis*-) acid yields a considerable amount of *iso*stilbene and a little stilbene, whilst the *allo*-(*trans*-)acid yields much stilbene together with some *iso*stilbene. From this it follows that *iso*stilbene (III) and stilbene (IV) have the *cis*- and the

(III.) PhCH·CH·CHPh (IV.) PhCH·CH·HCPh

trans-configurations respectively. This conclusion agrees with that of Straus (A., 1906, i, 77) and is contrary to that of Wislicenus.

The production of the *iso*stilbene during the decomposition of *allo*-α-phenylcinnamic acid by barium oxide is shown experimentally to be due to the conversion of the *allo*- into the *cis*-acid previous to the elimination of carbon dioxide. C. S.

Stereoisomeric 2-Nitro-α-phenylcinnamic Acids and Other Stilbene Derivatives. R. Stoermer and L. Prigge (*Annalen*, 1915, **409**, 20—35).—The stable 2-nitro-α-phenylcinnamic acid, m. p. 196° (*amide*, pale yellow needles, m. p. 173—174°; *anilide*, citron-yellow needles, m. p. 136°), and the *allo*-acid, m. p. 146—147° (*amide*, citron-yellow crystals, m. p. 166—167°; *anilide*, yellowish-white, crystalline powder, m. p. 148—149°), were prepared by Bakunin in 1895, but the latter was obtained in extremely small amounts. The authors now obtain it easily by exposing a concentrated aqueous solution of sodium 2-nitro-α-phenylcinnamate to the light of a Uviol lamp at a distance of 6—8 cm. for seven days. Since the *allo*-acid is stronger than acetic acid, the separation of the two stereoisomerides is easily effected by the addition of 50% acetic acid in the cold so long as the stable acid is precipitated. The filtrate is acidified with concentrated hydrochloric acid, and the precipitated *allo*-acid, after crystallisation from benzene, has m. p. 146—147° and is obtained in 10·7% yield; after twenty-one days' exposure the yield is 16%.

The *allo*-acid is so stable that it can scarcely be called labile. The only method of converting it into the stable isomeride is by exposing it in solution to a quartz lamp for forty-eight hours; even then the amount of the stable acid formed is less than 2%.

By the reduction of the stable 2-nitro-α-phenylcinnamic acid, Pschorr obtained the amino-acid in two modifications, one colourless and the other yellow. These are easily interconvertible, are not stereoisomeric, have the same m. p., 185—186°, and are readily converted into phenanthrene-9-carboxylic acid. They do not yield 3-*phenylcarbostyril* directly (preceding abstract), but this substance is obtained quantita-

tively when a benzene solution is exposed to a Uviol lamp; it crystallises in colourless needles, m. p. 227°. When 2-amino-α-phenylcinnamic acid is diazotised and boiled with water, the product contains, in addition to phenanthrene-9-carboxylic acid, a small amount of 3-phenylcoumarin. The substances $C_{16}H_{14}O_2$ and $C_{17}H_{14}O_2$, obtained by heating 2-methylphenanthrene-9-carboxylic acid and 4-methylphenanthrene-9-carboxylic acid (Mayer and Balle, A., 1914, i, 536), are phenylmethylcoumarins, $C_{16}H_{12}O_2$; the identity of the substance, m. p. 146—147°, from 2-methylphenanthrene-9-carboxylic acid with 3-phenyl-6-methylcoumarin has been proved by direct comparison.

4-Methoxy-α-phenylcinnamic acid (*amide*, leaflets, m. p. 131·5—132·5°) in the form of its sodium salt in aqueous solution is converted by exposure to a Uviol lamp for twenty-one days to the extent of 30% into the allo-*acid*, colourless crystals, m. p. 123°, which forms an *amide*, colourless needles, m. p. 168—169°, and an *aniline* salt,

$$C_{16}H_{14}O_3,NH_2Ph,$$

m. p. 116°, and is reconverted to the extent of 4·5% into the stable acid by exposing its solution in benzene containing a little iodine to the light of a quartz lamp for twenty-four hours.

If, as is probably the case, the stable 4-methoxy-α-phenylcinnamic acid has a configuration corresponding with that of the stable α-phenylcinnamic acid (preceding abstract), the *p*-methoxystilbene produced by its dry distillation should be the oily *allo*-modification; owing, however, to the high temperature of the decomposition, the *allo*-form undergoes transformation and the stable *p*-methoxystilbene, m. p. 135—136°, is actually obtained. By exposing its solution in benzene to the light of a Uviol lamp for fourteen days, the latter changes to allo-p-*methoxystilbene* to the extent of 45·7%. The *allo*-modification changes completely to the stable form at about 170°/15 mm., and even when distilled at 143—145°/1·5 mm. yields an oily distillate which slowly deposits crystals of the stable isomeride. *allo-p*-Methoxystilbene resembles *iso*stilbene in having a peculiar, sweet odour, which is not exhibited by the solid modification.

Stable *o*-nitrostilbene in benzene solution, exposed to a Uviol lamp for fourteen days, is partly converted into the allo-*isomeride*, citron-yellow crystals, m. p. about 42°. The reconversion into the stable modification has not been effected, and both isomerides yield the same stable aminostilbene, m. p. 106°, by reduction with stannous chloride and hydrochloric and acetic acids. C. S.

Stereoisomeric α-Substituted Cinnamic Acids. R. Stoermer and G. Voht (*Annalen*, 1915, **409**, 36—58. Compare preceding abstracts).—The most convenient method of preparing labile (*allo*-) α-phenylcinnamic acid, m. p. 137°, is to expose an aqueous solution of sodium α-phenylcinnamate to a Uviol lamp for about three weeks or in quartz tubes to a quartz lamp for three or four days. The unchanged stable acid is precipitated by acetic acid, and from the filtrate the labile acid is precipitated by dilute hydrochloric acid in 30% yield. The *amide* and *anilide* of the stable acid have m. p. 127° and 141° respectively, and of the labile acid, 167—168° and 179° respectively.

The labile acid is converted into the stable to the extent of about 50% when its solution in benzene containing a little iodine is exposed to a quartz lamp for twenty-four hours.

The stability of both acids is very nearly the same, and the two isomerides furnish one of the very few cases in which the two substances are mutually interconvertible by heat. The authors, however, have ascertained the conditions under which the "stable" acid is really stable; when it is heated at 260—270°/12—13 mm. for ten minutes the amount of the labile acid produced is too small to be detected, whilst the labile acid, heated at 250°/20 mm. for the same time, yields at least 20% of the stable acid.

allo-*α-Phenylcinnamonitrile*, b. p. 213—214°/23 mm., obtained in about 30% yield by exposing the stable nitrile in benzene solution to a Uviol lamp for three weeks, has a faint, sweet odour, and is converted into the solid, stable nitrile by distillation at the ordinary pressure.

allo-*α-Phenoxycinnamic acid*, slender needles, m. p. 73° (*amide*, colourless needles, m. p. 107°; *aniline* salt, m. p. 98—99°), is obtained by exposing an alcoholic solution of the stable acid (*amide*, stout needles, m. p. 172°) to a quartz lamp for forty-eight hours.

The best method of preparing α-phenoxy-4-methoxycinnamic acid (*amide*, colourless needles, m. p. 194°) is to esterify the mixture of this acid and *p*-methoxycinnamic acid obtained by the interaction of sodium phenoxyacetate, anisaldehyde, and acetic anhydride at 150°, fractionate the product, and hydrolyse the fraction, b. p. 220—240°/18 mm. The allo-*acid*, colourless needles, m. p. 120°, which forms an *amide*, m. p. 123—124°, and an *aniline* salt, m. p. 113°, is obtained when an aqueous solution of sodium α-phenoxy-4-methoxycinnamate in quartz tubes is exposed to a quartz lamp for forty-eight hours, the unchanged and the *allo*-acids being precipitated by 50% acetic acid and by hydrochloric acid respectively.

The two known modifications, m. p. 81—82° and 73—74° respectively, of α-methylcinnamic acid are dimorphous forms of one and the same stable acid, in which the phenyl and methyl groups are in the *cis*-position to one another. The two modifications behave alike chemically, form the same *methyl* ester, b. p. 137—138°/16 mm., m. p. 38—38·5°, and *phenylhydrazine* salt, m. p. 64—65° (but not an aniline salt), and cannot be converted into methylindone. Either of the two modifications in benzene solution is converted by the light of a quartz lamp into allo-*α-methylcinnamic acid*, stout, monoclinic crystals, m. p. 91—92°, which forms an *aniline* salt, m. p. 74—74·5°, *methyl* ester, b. p. 122°/16 mm., and *amide*, m. p. 137—138°, and is converted easily into 2-*methylindone*, $C_6H_4\langle\begin{matrix}CO\\CH\end{matrix}\rangle CMe$, yellow prisms, m. p. 47—47·5°, b. p. 119—120°/16 mm. (*semicarbazone*, deep yellow needles, m. p. 192—193° [decomp.]), by concentrated sulphuric acid at −2°.

In a similar manner, α-ethylcinnamic acid is converted into allo-*α-ethylcinnamic acid*, which has only been obtained in the form of an oily mixture of the two stereoisomerides. It forms an *aniline* salt, m. p. 81°, and is readily converted into 2-*ethylindone*, a yellow oil, which forms a *semicarbazone*, yellow needles, m. p. 181°. C. S.

Absorption Spectra of Various Phthalides and Related Compounds. II. DAVID S. PRATT and HARVEY C. BRILL (*Chem. Zentr.*, 1915, i, 834—835. Compare A., 1914, i, 415).—The absorption spectra of thiophthalic anhydride, dithiophthalimide, thiophthalanil, phthalaniloxime and its acetate, and thiophthaloxime, and its sulphate and acetate were examined in the usual solvents and also in concentrated sulphuric acid. From the absorption spectra of dithiophthalimide and thiophthaloxime an unsymmetric structure is deduced for phthaloxime, and further proof of this is seen in the fact that the production of colour by salt formation of the oximes of this type is not dependent on a molecular isomerism, but on alterations in the partial valence equilibrium. *Dithiophthalimide*, $C_6H_4<^{CS}_{CS}>NH$, prepared by heating phthalimide with phosphorus pentasulphide in xylene solution, forms red needles, m. p. 180° (corr.). *Phthalaniloxime acetate*, $C_6H_4<^{CO}_{C(N\cdot OAc)}>NPh$, prepared by the action of acetic anhydride on the oxime, forms colourless needles, m. p. 174°(corr.). *Thiophthaloxime*, $C_6H_4<^{CS}_{C(N\cdot OH)}>O$, from phthaloxime and phosphorus pentasulphide, forms long, red needles, m. p. 148·5°(corr., decomp.). *Thiophthaloxime sulphate*, $C_8H_5O_2NS,H_2SO_4$, yellow prisms, has m. p. 159° (corr., slight decomp.). The metallic salts of thiophthaloxime are strongly coloured, the ammonium and alkali salts being purple. In the presence of moisture they are converted into colourless salts of *thiophthalhydroxamic acid*, $C_6H_4<^{CS\cdot OH}_{C(N\cdot OH)\cdot OH}$. *Thiophthaloxime acetate* forms orange plates, m. p. 104° (corr.). G. F. M.

Phthalides of the Benzene, Naphthalene, and Carbazole Series. I. MAURICE COPISAROW and CHARLES WEIZMANN (T., 1915, **107**, 878—886).—The condensation of *o*-xylene with phthalyl chloride in the presence of aluminium chloride led to the formation of *o-xylylphthaloylic acid*, $CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_3Me_2$, and *di-o-xylylphthalide*, $(C_6H_3Me_2)_2C<^{C_6H_4}_{O}>CO$, a white, crystalline powder, m. p. 107—108°. Similarly, from α-ethoxynaphthalene was derived *o-1-ethoxynaphthoylbenzoic acid*, $CO_2H\cdot C_6H_4\cdot CO\cdot C_{10}H_5\cdot OEt$, white plates, m. p. 155—156°, and *di-1-ethoxynaphthylphthalide*,

$$(EtO\cdot C_{10}H_6)_2C<^{C_6H_4}_{O}>CO,$$

m. p. 159°, from which the ethoxy-groups were eliminated by heating with aluminium chloride, giving *α-naphthaphthalein*, brownish-yellow crystals, m. p. 209—210°. *α-Naphthafluorane* was obtained by fusing the phthalein for half-an-hour at 290°.

The action of phthalyl chloride or phthalic anhydride on 9-ethylcarbazole led to the formation of *9-ethylcarbazole-3-phthaloylic acid*, $CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_3<^{C_6H_4}_{NEt}$, white needles from benzene, m. p. 188—189°, and *9-ethylcarbazole-3 : 6-diphthaloylic acid*, rhombic crystals, m. p. 266—268°. On heating with concentrated sulphuric

acid it was converted into the corresponding quinone, 2 : 3 : 6 : 7-*diphthaloyl*-9-*ethylcarbazole*, a yellowish-grey substance which did not melt at 300°. The main product of the action of phthalyl chloride on 9-ethylcarbazole was *di*-9-*ethylcarbazylphthalide*,

$$(C_{12}H_7NEt)_2C<\begin{matrix}C_6H_4\\O\end{matrix}>CO,$$

a canary-yellow substance, decomp. above 155°. This was accompanied by some *tri*-9-*ethylcarbazyldiphthalide*, a light yellow, crystalline substance, decomp. above 235°. G. F. M.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXVIII. *o*-Carboxyphenylthiolacetic Acid. Rud. Wegscheider and Alice Joachimowitz (*Monatsh.*, 1914, **35**, 1037—1059).—In accordance with the rules already given for the esterification of polybasic acids, the authors find, in the case of *o*-carboxyphenylthiolacetic acid, $CO_2H\cdot C_6H_4\cdot S\cdot CH_2\cdot CO_2H$, that the carboxyl group situated in the side-chain undergoes esterification with methyl alcohol and hydrogen chloride or sulphuric acid much more readily than the nuclear carboxyl, whilst, on partial hydrolysis with aqueous hydrochloric acid, the dimethyl ester is converted into the acid ester, in which the nuclear carboxyl remains esterified.

No definite conclusions could be drawn from the partial hydrolysis of the dimethyl ester with aqueous alkalis or ammonia, owing to the ease with which it is transformed even at the ordinary temperature and with very small concentrations of alkali into methyl 2-hydroxythionaphthen-1-carboxylate, $C_6H_4<\begin{matrix}C(OH)\\S\end{matrix}>C\cdot CO_2H$ (compare Friedländer, A., 1907, i, 335). It is worthy of note that the acid ester, $CO_2Me\cdot C_6H_4\cdot S\cdot CH_2\cdot CO_2H$, cannot be converted by the influence of alkalis into a thionaphthen derivative.

The action of methyl iodide on the potassium hydrogen salt of *o*-carboxyphenylthiolacetic acid gives rise to *o*-methylthiolbenzoic acid, $SMe\cdot C_6H_4\cdot CO_2H$, and its methyl ester.

A similar loss of carbon dioxide, resulting in the formation of the latter two substances, also occurs when the neutral silver salt is treated with methyl iodide at the ordinary temperature, or the free acid heated with silver oxide and methyl iodide in methyl-alcoholic solution on the water-bath. Since neither the free acid nor the potassium hydrogen salt loses carbon dioxide when heated under similar conditions in the absence of methyl iodide, the author suggests that an intermediate sulphonium iodide (I) is formed in the reaction, and it is either from this compound or from its transformation product (II) that the loss of carbon dioxide occurs, as represented in the following scheme :

$$CO_2H\cdot C_6H_4\cdot S\cdot CH_2\cdot CO_2H \xrightarrow{MeI} (I.)\ CO_2H\cdot C_6H_4\cdot SMeI\cdot CH_2\cdot CO_2H \longrightarrow$$

$$HI + (II.)\ CO<\begin{matrix}O\\C_6H_4\end{matrix}>SMe\cdot CH_2\cdot CO_2H \xrightarrow{-CO_2} (III.)\ CO<\begin{matrix}O\\C_6H_4\end{matrix}>SMe_2.$$

The compound (III) then undergoes rearrangement into methyl *o*-methylthiolbenzoate, and at the same time is partly converted into *o*-methylthiolbenzoic acid by the hydrogen iodide simultaneously produced in the reaction. An alternative explanation, based on the

tendency of bivalent sulphur to combine with methyl iodide, without necessarily forming definite intermediate sulphonium compounds, is also offered.

The *monopotassium* salt of *o*-carboxyphenylthiolacetic acid is obtained as a yellow, crystalline powder by the addition of the calculated amount of potassium hydroxide to the acid in methyl-alcoholic solution; the *disilver* salt is also described; the *dimethyl* ester obtained by direct esterification of the acid with methyl alcohol and hydrogen chloride forms triclinic crystals ($a:b=1:4{\cdot}693$), m. p. 50—51°, and is transformed by aqueous or alcoholic alkalis into methyl 2-hydroxythionaphthen-1-carboxylate, triclinic crystals ($a:c=1:0{\cdot}5306$), m. p. 107—108° (Friedländer gives 104°).

If the esterification is incomplete, the *monomethyl* ester,

$$CO_2H{\cdot}C_6H_4{\cdot}S{\cdot}CH_2{\cdot}CO_2Me,$$

is also produced. This forms a white, crystalline powder, m. p. 126—127·5°, and is more readily hydrolysed by aqueous potassium hydroxide than the isomeric ester, $CO_2Me{\cdot}C_6H_4{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, which may be prepared by partial hydrolysis of the dimethyl ester with hydrochloric acid.

On treatment with aqueous ammonia (2*N*) at the ordinary temperature the dimethyl ester gives rise to methyl 2-hydroxythionaphthen-1-carboxylate and the *ammonium* salt of the latter ester, which has m. p. 105—108°. After drying over sulphuric acid the ammonium salt has the composition $2C_{10}H_8O_3S,NH_3$, but whether this represents the composition of the original salt has not yet been decided. When boiled with benzene or chloroform the ammonium salt in converted by loss of ammonia into methyl 2-hydroxythionaphthen-1-carboxylate, from which it may be directly prepared. F. B.

Formation of Ellagic Acid from Galloylglycine by Penicillium. Maximilian Nierenstein (*Biochem. J.*, 1915, **9**, 240—244).—The isolation of galloyl-leucine from oak galls (A., 1914, i, 1041) suggested that the digallic acid nucleus in tannic acid may be built up from such nitrogenous products. The action of *Penicillium* on galloylglycine has been studied, in the expectation that digallic acid might be produced, but the product after three weeks' incubation is found to be the stable oxidation product of this, namely, ellagic acid. It is supposed to be formed according to the scheme:

$$2C_6H_2(OH)_3{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H + O + 2H_2O = \begin{matrix} O{-}C_6H(OH)_2{\cdot}CO \\ | \qquad\qquad | \\ CO{\cdot}C_6H(OH)_2{\cdot}O \end{matrix} + 3H_2O + 2NH_2{\cdot}CH_2{\cdot}CO_2H.$$

Glycine was converted by tricarbomethoxygalloyl chloride (Fischer, A., 1908, i, 892) into *tricarbomethoxygalloylglycine* [3 : 4 : 5-*trimethylcarbonatobenzoylaminoacetic acid*], $(CO_2Me{\cdot}O)_3C_6H_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, prismatic needles, m. p. 202—204° (decomp.), and this was hydrolysed by dilute pyridine to *galloylglycine* [3 : 4 : 5-*trihydroxybenzoylaminoacetic acid*], $C_9H_9O_6N$, cubes, m. p. 282—283°. J. C. W.

"Thiosaccharin" [Thio-*o*-benzoicsulphinide]. Anna Mannessier (*Gazzetta*, 1915, **45**, i, 540—552).—It has been previously shown

(compare Oddo and Mannessier, A., 1910, i, 399; Mannessier, A., 1914, i, 1127) that the carbonylic oxygen of camphorimide and chlorocamphorimide is readily replaced by sulphur under the action of phosphorus pentasulphide. The author now finds that the latter also acts on *o*-benzoicsulphinide at 220°, yielding thio-*o*-benzoicsulphinide, which usually yields *o*-benzoicsulphinide and hydrogen sulphide when hydrolysed. This reaction is effected by prolonged boiling with water or by alkali in the cold; the *o*-benzoicsulphinide thus formed is transformed by hot alkalis into *o*-sulphoaminobenzoic acid. Ammonia solution, either hot or cold, dissolves the compound, giving a pale yellow solution, from which thio-*o*-benzoicsulphinide is precipitated unchanged on acidification. The action of dilute acid results in the formation, first of *o*-benzoicsulphinide and then of ammonium *o*-sulphobenzoate (compare Krannich, A., 1901, i, 153). Concentrated nitric acid yields a nitro-derivative, which is being further investigated, as also is an intensely red, non-nitrogenous compound, m. p. 98°, formed along with the thio-*o*-benzoicsulphinide.

Thio-o-benzoicsulphinide, $C_6H_4<^{CS}_{SO_2}>NH$, forms yellow needles, m. p. 180°, having a very bitter taste; it is obtained in 90% yield only when about 3 grams of the *o*-benzoicsulphinide are taken, the yield vanishing when 10 grams are employed. For the estimation of the sulphur content it is necessary to use an excess of nitric acid in presence of barium nitrate and to heat the mixture in a sealed tube for three hours at each of the temperatures, 180—190°, 240—250°, and about 300° (compare Anelli, A., 1911, ii, 533). Treatment with acetic anhydride yields acetyl-*o*-benzoicsulphinide, which, like the same compound obtained from acetic anhydride and *o*-benzoicsulphinide, has m. p. 198°; Eckenroth and Koerppen (A., 1896, i, 438) found m. p. 193°. The action of cold concentrated nitric acid gives a pale yellow, amorphous, nitrogenous compound, m. p. 205—210°, insoluble in all organic solvents.

The *ammonium* derivative, $C_6H_4<^{CS}_{SO_2}>N\cdot NH_4$, forms slender, straw-yellow needles, and in aqueous solution gives with copper acetate a brown, with lead acetate a white, with ferric chloride a yellow, precipitate; salts of the alkaline earth metals give white, and those of the alkali metals, straw-yellow, precipitates. The *silver* derivative, $C_7H_4O_2NS_2Ag$, forms a pale yellow precipitate, m. p. 250—255°, blackening in the light; the *mercury* derivative, $C_7H_4O_2NS_2Hg$, a white, curdy precipitate, blackening in the light; the *sodium* derivative, straw-yellow scales; the *pyridine* derivative, $C_{12}H_{11}O_2N_2S_2$, stellar aggregates of greenish-yellow, pyramidal crystals, m. p. 152°, and *methylthio-o-benzoicsulphinide*, $C_6H_4<^{CS}_{SO_2}>NMe$, colourless prisms, m. p. 221°, with an insipid taste. T. H. P.

Constitution of the Salts of Phenol-aldehydes. H. Pauly (*Ber.*, 1915, **48**, 934—937. Compare A., 1911, i, 787).—A reply to Hantzsch (*Ber.*, 1915, **48**, 815). J. C. W.

Homovanillin. C. HARRIES (*Ber.*, 1915, **48**, 868—869. Compare this vol., i, 133).—The homovanillin which was described as an oil has been repeatedly fractionated until a solid specimen, b. p. 105—106°/0·25 mm., was obtained. By inoculating the crude oils with this, a quantity of the solid substance was prepared. Homovanillin forms glistening white, stout prisms or leaflets, m. p. 50—50·5°, and the pure *p*-nitrophenylhydrazone has m. p. 154·5°. J. C.W.

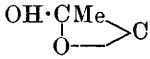
The Course of the Reaction between Aromatic Aldehydes and Dimethyl Diketone Monoxime in the Presence of Concentrated Hydrochloric Acid. OTTO DIELS and DONALD RILEY (*Ber.*, 1915, **48**, 897—905).—It was previously shown that dimethyl diketone monoxime condenses with benzaldehyde and furfuraldehyde in the presence of a concentrated alkali hydroxide to form oximes of unsaturated $\alpha\beta$-diketones (A., 1913, i, 875). Under these conditions, anisaldehyde does not react at all. Condensation with dimethyl diketone monoxime takes place, however, in the presence of concentrated hydrochloric acid, but the properties of the product are not what was expected. Benzaldehyde also gives a different condensation product under these conditions. Instead of being feebly acid, the compounds are weak bases and form crystalline salts which are dissociated by water. The reactions agree with a formula of a new type, $RC\begin{smallmatrix}O\cdot CMe\\ \|\\ N\cdot CMe\end{smallmatrix}>O$.

Dimethyl diketone monoxime, anisaldehyde, and concentrated hydrochloric acid were shaken together for twenty hours, and then the white mass which separated was filtered, dissolved in about 0·1*N*-hydrochloric acid, filtered again, and the filtrate was rendered alkaline.

The *compound*, $OMe\cdot C_6H_4\cdot C\begin{smallmatrix}O\cdot CMe\\ \|\\ N\cdot CMe\end{smallmatrix}>O$, separated as a mass of very long, slender, colourless needles, m. p. 72—80°, which lost water of crystallisation in a vacuum desiccator, and then had m. p. 140—141°, and was sensitive to light. The substance was boiled with zinc dust and water, and the product was extracted with ether and distilled under reduced pressure, in a special flask and receiver (figured in the text), since the distillate crystallised so readily. The reduction *product*, $OMe\cdot C_6H_4\cdot C\begin{smallmatrix}O\cdot CMe\\ \|\\ N\cdot CMe\end{smallmatrix}$, has b. p. 175°/11 mm., m. p. 71—72°, is a weak base, does not react with ammonia, aniline or phenylhydrazine, but is vigorously attacked by hot, dilute nitric acid.

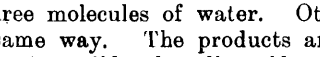
The substance also reacted with phenylcarbimide in ether, under evolution of gas, to give a *compound* which is believed to have the structure $OMe\cdot C_6H_4\cdot C\begin{smallmatrix}O\cdot CMe\\ \|\\ N\cdot CMe\end{smallmatrix}>NPh$, for it could not be reduced, and the above reduction product did not combine with the reagent. The substance has m. p. 164—165°, and is accompanied by dimethyl diketone and diphenylcarbamide as by-products.

The original compound suffers great change when warmed with aniline at 100°. The *product* has m. p. 164°, and is accorded the

structure  , for it is very readily hydrolysed by dilute acids to dimethyl diketone, aniline, ammonia, and anisic acid. When warmed with 5% oxalic acid, it also loses dimethyl diketone and forms the *oxalate* of an unstable amidine, $C_{16}H_{16}O_5N_2,2H_2O$, large crystals, m. p. 157°, which yields aniline and anisamide on rubbing with sodium hydrogen carbonate solution.

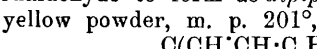
The corresponding compounds in the case of benzaldehyde are, the *condensation product*, $C_{11}H_{11}O_2N$, long needles, m. p. 58—62° (hydrated), 100—101° (anhydrous); its *reduction product*, $C_{11}H_{11}ON$, m. p. 50—55°, b. p. 147°/11 mm.; and its *derivative* with aniline, $C_{17}H_{18}O_2N_2$, m. p. 150°, which gave dimethyl diketone when warmed with oxalic acid, and an oxalate which yielded benzamide and aniline with sodium hydrogen carbonate. J. C. W.

Condensation of γ-Ketonic Acids with Aldehydes. II. W. Borsche (*Ber.*, 1915, **48**, 842—849. Compare A., 1914, i, 686).—Since sodium β-benzoylpropionate and benzaldehyde in the presence of acetic anhydride yield γ-phenyl-α-benzylidenecrotonolactone (*loc. cit.*), it was expected that sodium lævulate would yield, under the same conditions, α-benzylideneangelolactone, but it was found that two molecules of each condense with the elimination of three molecules of water. Other aromatic aldehydes behave in the same way. The products are no longer acids or ketones, but yield α-benzylidenelævulic acids on hydrolysis. They are, therefore, anhydrides, and, at the same time, dilactones of these acids.

The simplest member, the *lactone anhydride* of *α-benzylidenelaevulic acid*,  , could only be obtained in small quantity, as yellow needles, m. p. 108—109°. Better results were realised when dry sodium lævulate, acetic anhydride, and anisaldehyde were heated on the water-bath for twelve hours. The *lactone anhydride* of *α-anisylidenelaevulic acid*, $C_{26}H_{26}O_7$, formed long, yellow needles, m. p. 137—138°. This was converted into α-anisylidenelævulic acid (Thiele, Tischbein, and Lossow, A., 1902, i, 155), which condensed with anisaldehyde to form αδ-dianisylidenelævulic acid (*loc. cit.*). The ethyl ester of the above acid was characterised by a *semicarbazone*, $C_{16}H_{21}O_4N_3$, white leaflets, m. p. 203—204°.

The corresponding *lactone anhydride* of *α-piperonylidenelaevulic acid*, $C_{56}H_{22}O_9$, crystallised in orange-yellow needles, m. p. 187°. This was hydrolysed to *α-piperonylidenelaevulic acid*,

$$CH_2O_2{:}C_6H_3{\cdot}CH{:}C(CH_2Ac){\cdot}CO_2H,$$

pale yellow, stout prisms, m. p. 125—126°, and the corresponding *ethyl* ester, m. p. 84—85°, which formed a *semicarbazone*, $C_{16}H_{19}O_5N_3$, white leaflets, m. p. 212° (decomp.). The acid condensed with more piperonaldehyde to form *αδ-dipiperonylidenelaevulic acid*, $C_{21}H_{16}O_7$, a pale yellow powder, m. p. 201°, which yielded *αδ-dipiperonylidene-angelolactone*,  , reddish-brown needles,

m. p. 260—261°, when heated above its m. p. This lactone is more conveniently prepared by condensing piperonaldehyde with lævulic acid in the presence of dilute aqueous alcoholic sodium hydroxide to *δ-piperonylidenelaevulic acid*, m. p. 150°, and heating the sodium salt of this with acetic anhydride and piperonaldehyde.

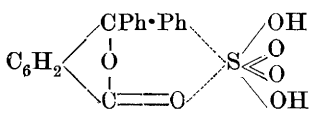
The *lactone anhydride* of *α-cinnamylidenelaevulic acid*, $C_{28}H_{26}O_5$, crystallised in yellowish-red needles, m. p. 166°, and was hydrolysed to *α-cinnamylidenelaevulic acid*, $CHPh{:}CH{\cdot}CH{:}C(CH_2Ac){\cdot}CO_2H$, pale yellow needles, m. p. 154—155°, and the corresponding *ethyl* ester, m. p. 62—63°. The acid condensed with anisaldehyde to *α-cinnamylidene-δ-anisylidenelaevulic acid*, $C_{22}H_{20}O_4$, pale yellow needles, m. p 233—234°, but this was more easily obtained by the hydrolysis of the corresponding angelolactone (*loc. cit.*). J. C. W.

Preparation of a Ketone with Musk-like Odour from Civet. Erwin Sack (D.R.-P. 279313).—Civet is boiled with concentrated alcoholic alkali for some hours, the solvent is removed, the residue diluted with water, and extracted with ether. This extract is evaporated and the residue is distilled with steam until all the scatole (and such like) is removed, when the non-volatile residue is extracted with a suitable solvent and the soluble ketone is purified as the semicarbazone. As an alternative, civet is distilled with concentrated alkali hydroxide and the oily distillate is treated as above. In this way an additional constituent of civet with a jasmine odour is recovered.

The ketone is not identical with muskone (compare Walbaum, A., 1906, i, 595). It is designated *zibethone*, has the formula $C_{17}H_{30}O$, forms transparent spear-shaped crystals, m. p. 32·5°, b. p. 204—205°/17 mm., and yields a *semicarbazone*, $C_{18}H_{33}ON_3$, pearly leaflets or white needles, m. p. 187°, and an *oxime*, m. p. 92°. J. C. W.

Absorption Spectra of Certain Phthalides and Related Substances. David S. Pratt (*Chem. Zentr.*, 1914, ii, 473).—The absorption spectra of the following substances in the usual solvents and in concentrated sulphuric acid have been investigated: phthalic acid, phthalic anhydride, maleic anhydride, phthalide, phthalimide, phthalimidine, nitrosophthalimidine, benzylidenephthalide, cyanobenzylidenephthalide, phthalylacetic acid, diphthalyl, phthalanil, phthalophenone, phthalophenoneanilide, and phthaloxime. In the original, the results are given in a series of diagrams.

The author is led to the conclusion that the transformation of a colourless into a coloured solution, as well as the alteration in colour of the compounds investigated, cannot always be explained by the quinonoid theory. For example, it is improbable that phthalophenone has a true quinonoid structure in concentrated sulphuric acid. The assumption of a union between the sulphuric acid and the latent valencies of the unsaturated phenyl and carbonyl groups appears more probable. Such a theory has been advanced in the case of the alkali salts of phthaloxime (Pratt and Gibbs, A., 1914, i, 415); in the present instance, instead of a metallic atom being introduced into the ring, the solvent is added, yielding a product (annexed



formula). A similar structure can be advanced for solutions of phthaleins in sulphuric acid without the assumption of a quinonoid transformation. The compound formed with sulphuric acid is unstable and is decomposed by the addition of water.

Investigations with thio-derivatives give similar results which are to be published later. The introduction of nitrogen in place of oxygen into the molecule diminishes in every case the action of sulphuric acid; consequently, the absorption spectra in acid and in alcoholic solution are very similar. H. W.

Keto-dilactone of Benzophenone-2 : 4 : 2′ : 4′-tetracarboxylic Acid. W. H. MILLS (*Proc. Camb. Phil. Soc.*, 1915, **18**, 149—150).—This work was undertaken with a view to the preparation of compounds of the type $<^{a}_{b}>C<^{a}_{b}>$ which should be capable of resolution into their optically active components.

When di-*m*-xylyl ketone is heated with dilute nitric acid for about seventy hours, a mixture of dimethylbenzophenonedicarboxylic and other acids is produced which, on oxidation with alkaline potassium permanganate, gives a good yield of *benzophenone-2 : 4 : 2′ : 4′-tetracarboxylic acid*, $CO[C_6H_3(CO_2H)_2]_2$. When this acid is heated on the water-bath with hydrochloric acid, the *keto-dilactone*,

$$CO<^{C_6H_3(CO_2H)}_{\text{——O——}}>C<^{\text{——O——}}_{C_6H_3(CO_2H)}>CO,$$

m. p. 410°, is obtained as a heavy, crystalline powder, which is converted by phosphorus pentachloride into the *acid chloride*,

$$C_{15}H_6O_4(COCl)_2.$$

From the latter, the *ethyl* ester, m. p. 212°, and *bornyl* ester, m. p. 245°, have been prepared.

On reducing benzophenone-2 : 4 : 2′ : 4′-tetracarboxylic acid with zinc dust and ammonia, benzhydrol-2 : 4 : 2′ : 4′-tetracarboxylic acid is produced which, when liberated from its salts, passes rapidly into the corresponding *lactone*, $C_6H_3(CO_2H)_2\cdot CH<^{\text{——O——}}_{C_6H_3(CO_2H)}>CO$, m. p. 311°. E. G.

Intramolecular Transposition in the α-Glycols. S. A. KOOPAL (*Rec. trav. chim.*, 1915, **34**, 115—178. Compare Montagne and Koopal, A., 1910, i, 323).—The first part of the paper is a résumé of work already published on this subject. The author has examined the influence of the character and position of the halogen atoms in symmetric, dihalogenated benzopinacones on the pinacolin transposition. The pinacones studied were *s*-4 : 4′-di-iodo-, *s*-4 : 4′-difluoro-, *s*-3 : 3′-dichloro-, *s*-3 : 3′-dibromo-, *s*-2 : 2′-dichloro- and *s*-2 : 2′-dibromo-benzopinacones, all of which were prepared by reducing the corresponding ketones, which were obtained by Friedel and Crafts' reaction.

4-*Fluorobenzophenone*, m. p. 52°, was obtained by heating *p*-fluorobenzoyl chloride and aluminium chloride in carbon disulphide at 45° and then adding benzene. The impurities were removed by distillation with steam. s-2 : 2′-*Dichlorobenzopinacone*,

$$C_6H_4Cl\cdot CPh(OH)\cdot CPh(OH)\cdot C_6H_4Cl,$$

m. p. 178°, was obtained by the reduction of *o*-chlorobenzophenone either by alcohol in sunlight or in the light from a mercury lamp, or, better, by zinc and acetic acid. If the reduction was by sodium amalgam acting on an alcoholic solution, the product was *2-chlorobenzhydrol*, small needles, m. p. 65°. *m*-Chlorobenzophenone, when reduced under similar conditions, yielded respectively *s*-3 : 3′-*dichlorobenzopinacone*, m. p. 137—138°, and *3-chlorobenzhydrol*, m. p. 40°. s-2 : 2′-*Dibromobenzopinacone*, m. p. 168°, and *2-bromobenzhydrol*, m. p. 56°, were similarly obtained from *o*-bromobenzophenone. *m*-Bromobenzophenone yielded s-3 : 3′-*dibromobenzopinacone*, m. p. 147°, but the corresponding bromobenzhydrol was not obtained. *p*-Iodobenzophenone could only be satisfactorily reduced by zinc and acetic acid, when it yielded s-4 : 4′-*di-iodobenzopinacone*, m. p. 171—172°. *p*-Fluorobenzophenone, when reduced either by alcohol in sunlight or the light from a mercury lamp or by zinc and acetic acid, gave an almost theoretical yield of s-4 : 4′-*difluorobenzopinacone*, m. p. 176·5°. When reduced in alcoholic solution with sodium amalgam, it gave *4-fluorobenzhydrol*, m. p. 48°. All of these pinacones gave a blue colour with alcoholic potassium hydroxide, and they were all converted into their corresponding pinacolins by heating with acetyl chloride in a sealed tube at 100°. s-2 : 2′-Dichlorobenzopinacone yielded only the *β-pinacolin*, $C_6H_4Cl\cdot CPh_2\cdot CO\cdot C_6H_4Cl$, m. p. 138°. *s*-2 : 2′-Dibromobenzopinacone gave the *β-pinacolin*, $C_6H_4Br\cdot CPh_2\cdot CO\cdot C_6H_4Br$, m. p. 124°. *s*-3 : 3′-Dichlorobenzopinacone gave only the *β-pinacolin*, $C_6H_4Cl\cdot CPh_2\cdot CO\cdot C_6H_4Cl$, m. p. 107°, and *s*-3 : 3′-dibromobenzopinacone gave only the *β-pinacolin*, $C_6H_4Br\cdot CPh_2\cdot CO\cdot C_6H_4Br$, m. p. 115—116°. *s*-4 : 4′-Di-iodobenzopinacone yielded a mixture of the two pinacolins : $C_6H_4I\cdot CPh_2\cdot CO\cdot C_6H_4I$ (50%) and $COPh\cdot CPh(C_6H_4I)_2$ (50%). 4 : 4′-Difluorobenzopinacone similarly gave a mixture of the pinacolins : $C_6H_4F\cdot CPh_2\cdot CO\cdot C_6H_4F$ (35%) and $COPh\cdot CPh(C_6H_4F)_2$ (65%). W. G.

Spirans. VI. The *α*-Halogenation of Optically Active Ketones. Hermann Leuchs (*Ber.*, 1915, **48**, 1015—1020).—The fact that in the bromination of *d*-1-hydrindone-2-benzyl-*o*-carboxylic acid the product is at least in part optically active (Leuchs, A., 1913, i, 974; this vol., i, 411) leads the author to reject the view that such bromination takes place solely through the intervention of the enolic form of the substance. Similar chemical evidence is now forthcoming from the behaviour of the same substance on chlorination.

[With L. Lock.]—The chlorination of *dl*-1-hydrindone-2-benzyl-*o*-carboxylic acid in chloroform solution yields a product, m. p. 146—147° (decomp.). When the *d*-acid was chlorinated in a similar manner, the product was optically active and contained approximately $7\frac{1}{2}$% of the free dextro-form; repeated crystallisation from acetic acid gave pure d-*2-chloro*-1-*hydrindone*-2-*benzyl*-o-*carboxylic acid*,

$$C_6H_4<\begin{matrix}CH_2\\CO\end{matrix}>CCl\cdot CH_2\cdot C_6H_4\cdot CO_2H,$$

prisms, m. p. 171—173° (decomp.), $[\alpha]_D^{20}$ +130° in acetic acid; during the process of recrystallisation a solution was obtained which was

supersaturated with respect to the l-*isomeride*, and subsequently gave a deposit of this, m. p. 173°, $[\alpha]_D^{20}$ −129·4°.

When heated to the m. p. or treated with sodium carbonate solution both these isomerides underwent conversion into the corresponding lactones, $C_6H_4<\begin{matrix}CH_2\\CO_2\end{matrix}>C<\begin{matrix}CH_2\\CO\end{matrix}>C_6H_4$, with loss of hydrogen chloride; the *d*-acid thus yielded *l*-1-dihydro*iso*coumarin-1-hydrindone-3 : 2-spiran (*loc. cit.*), whilst the *l*-acid gave the corresponding *d*-spiran.

D. F. T.

Interaction of Benzoyldehydracetic Acid with Ammonia, Amines, and other Nitrogenous Compounds. IV. SCHÖTTLE (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 645—679).—Most of the results here described have been already published (Petrenko-Kritschenko and Schöttle, A., 1911, i, 1020; 1912, i, 128; Schöttle, A., 1912, i, 915; 1914, i, 408, 840).

The following further lactam derivatives have been prepared. The *heptylamine* derivative, $C_{25}H_{27}O_3N$, forms crystals, m. p. 83—84°; *allylamine* derivative, $C_{21}H_{17}O_3N$, crystals, m. p. 143—144°; *α-naphthylamine* derivative, $C_{28}H_{19}O_3N$, yellow crystals, m. p. 215—216°; *β-naphthylamine* derivative, crystals, m. p. 243—245°.

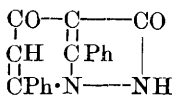
The *semicarbazide* derivative, $CO<\begin{matrix}CH{=}CPh\\CHBz\cdot CO\end{matrix}>N\cdot NH\cdot CO\cdot NH_2$, forms crystals, m. p. 180° (decomp.), and exhibits pronounced acid properties. With concentrated alcoholic potassium hydroxide solution, it yields carbamic acid and the compound,

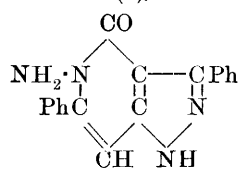
$$CO<\begin{matrix}CH{=}CPh\\CHBz\cdot CO\end{matrix}>N\cdot NH_2,$$

which then undergoes further change into

$$NH_2\cdot NH\cdot CPh{:}CH\cdot CO\cdot C(CO_2K){:}CPh\cdot OH \longrightarrow CO<\begin{matrix}CH{=}CPh\\C(CO_2K){:}CPh\end{matrix}>N\cdot NH_2$$

this carboxylic acid is stable only in the form of salts, and in the free state loses the elements of water, giving the *lactam* (I), which forms

(I.) 

(II.) 

crystals, m. p. 160—161°, and gives a deep violet colour with ferric chloride.

With hydrazine, benzoyldehydracetic acid reacts as with phenylhydrazine, giving the *compound* (II), which forms crystals, m. p. 280—281°, gives a deep cinnamon-brown coloration with ferric chloride, and resists prolonged heating with potassium hydroxide or hydrochloric acid.

Dimethylamine does not react with benzoyldehydracetic acid in the

cold, but, when heated with it in a sealed tube, yields the *compound*, $NMe_2 \cdot CPh{:}CH \cdot CO \cdot C(:CPh \cdot NMe_2) \cdot CO \cdot NMe_2$, which forms snow-white crystals, m. p. 218—219°, and gives no coloration with ferric chloride. It forms a *hydrochloride*, m. p. 228—230° (decomp.), and a *platinichloride*, $(C_{24}H_{29}O_2N_3)_3,4HCl,2PtCl_4$, but does not react with phenylhydrazine, hydroxylamine, or amines. When heated in a sealed tube with concentrated hydrochloric acid at 120—125°, it loses successively dimethylamine and benzoic acid, thus: $NMe_2 \cdot CPh{:}CH \cdot CO \cdot CHBz \cdot CO \cdot NMe_2 \longrightarrow NMe_2 \cdot CPh{:}CH \cdot CO \cdot CH_2 \cdot CO \cdot NMe_2$. The latter *compound*, m. p. 208—210°, yields a *platinichloride*, $(C_{15}H_{20}O_2N_2)_2,H_2PtCl_6$.

Diethylamine reacts with benzoyldehydracetic acid only with difficulty, and diphenylamine does not react, either in the cold or on heating in a sealed tube. T. H. P.

*iso*Quercetone. Maximilian Nierenstein. (T., 1915, **107**, 869—872).—Hydroxyquercetin yields on oxidation with *p*-benzoquinone an ortho-quinone, iso*quercetone*, analogous to the similar oxidation product, gossypetone, obtained from gossypetin (Perkin, T., 1913, **103**, 661). *iso*Quercetone resembles gossypetone in general properties and colour reactions, but differs somewhat in its dyeing qualities. The following derivatives are described: *Tetramethyl ether*, $C_{15}H_4O_4(OMe)_4$, prepared by the action of the theoretical quantity of diazomethane on *iso*quercetone, forms yellow needles, m. p. 242—244°, and condenses with tolylene-3 : 4-diamine to form an *azine*, $C_{26}H_{22}O_6N_2$, m. p. 328—331° (decomp.). 7 : 8-*Methylenedioxy*-3 : 5 : 3′ : 4′-*tetramethoxyflavone* is formed when an excess of diazomethane is employed in the above reaction. It forms yellow, prismatic needles, m. p. 192—193°, and elimination of the methylene group leads to the production of 7 : 8-*dihydroxy*-3 : 5 : 3′ : 4′-*tetramethoxyflavone*, identified by conversion into hexamethoxyflavone. *Tetra-acetyl*iso*quercetone* forms prismatic needles, m. p. 240—242°.

G. F. M.

New Class of Coloured Reduction Products of 1-Benzoylanthraquinones and of 2 : 3-Phthaloylbenzophenones. I. Alfred Schaarschmidt (*Ber.*, 1915, **48**, 973—978).—It has recently been shown (Schaarschmidt, this vol., i, 566) that whereas the 2-benzoylanthraquinones undergo reduction to colourless anthranol derivatives, the isomeric 1-benzoyl compounds give rise to blue or bluish-violet substances which dissolve in alkaline sodium hyposulphite to red solutions. This new class of coloured reduction product is now examined more closely.

When 1-*p*-chlorobenzoylanthraquinone (1 mol.) is treated in solution in sulphuric acid with sufficient aluminium "bronze" to supply an atomic proportion of hydrogen, the solution rapidly becomes green and shortly deposits green needles of a substance which is converted by water into a violet-blue solid, $C_{21}H_{12}O_3Cl$, m. p. 220—222°. This blue compound appears to stand in close relationship with the intermediate green product, and its solution in sulphuric acid by cautious dilution

can be made to regenerate the green compound, whereas further dilution again yields the blue compound. The blue substance dissolves sparingly in most solvents, its solutions in solvents containing a hydroxylic, carboxylic or amino-group possessing a blue colour, whilst those in hydrocarbons, tertiary amines, and acetic anhydride are red with a red fluorescence; the latter type of solution is much more sensitive to light than the former. The formula

$$\left[C_6H_4\begin{<}{CO\\CO}\begin{>}C_6H_3\cdot C(OH)(C_6H_4Cl)\cdot\right]_2$$

is suggested for the blue compound, attention being drawn to the possibility that the intense colour may be due in part to the formation of subsidiary cyclic systems by means of partial valencies between the ketonic and hydroxylic groups. D. F. T.

Preparation of Nitrogenous Condensation Products of the Anthraquinone Series. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 269749).—When the condensation of 4-chloro-1-aminoanthraquinone with β-naphthol in the presence of zinc chloride is carried out at 180—190°, the product is different from that obtained at 200—220° (A., 1913, i, 1368), being a dark purple, crystalline powder, which is very soluble in pyridine and contains a very reactive chlorine atom. J. C. W.

Preparation of Thiocarbamides of the Anthraquinone Series. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 271745).—It is found that aminoanthraquinones with at least one amino-group in the β-position react very readily with carbon disulphide when boiled together in an indifferent solvent like pyridine. Thus 2-aminoanthraquinone yields di-2-anthraquinonylthiocarbamide, small, yellow needles, which dyes cotton in the vat an orange-yellow shade and dissolves in concentrated sulphuric acid with a dark brown colour which soon pales, when the final solution deposits a more red dye on dilution. 1 : 2-Diaminoanthraquinone gives a reddish-brown dye in glistening needles; 2 : 3-diaminoanthraquinone yields a yellow dye, and 1 : 2 : 4-triaminoanthraquinone forms a lustrous dye which gives brownish-violet shades. J. C. W.

New Method of Preparing Cyclic Ketones. II. ALFRED SCHAARSCHMIDT (*Annalen*, 1915, **409**, 59—78. Compare A., 1914, i, 732).—The method of preparing acridone derivatives, by the reaction between an aromatic amine and an aromatic nitrile containing a halogen atom in the ortho-position and treatment of the resulting *o*-cyanodiphenylamine derivative with a reagent which simultaneously effects hydrolysis and condensation, has been amplified to include the preparation of thioxanthones of the anthraquinone series. The requisite aromatic sulphides, which must contain a cyano-group in the ortho-position in one nucleus and an unsubstituted ortho-position in the other, belong to a hitherto unknown class of compounds, but representatives in the anthraquinone series can be obtained with

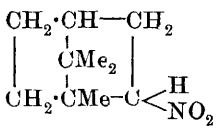
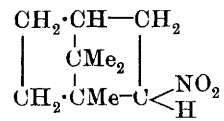
astonishing ease by treating a suspension of 2-bromo-1-cyanoanthraquinone and an aromatic mercaptan in boiling amyl alcohol with potassium carbonate for half an hour; when "fenchosol" is employed as a solvent the reaction is finished in one to two minutes. In this manner *p*-tolyl mercaptan yields 1-*cyano*-2-p-*tolylthiolanthraquinone*, $C_6H_4{:}(CO)_2{:}C_6H_2(CN)\cdot S\cdot C_6H_4Me$, faintly yellow needles, m. p. 251°; 1-thiolanthraquinone yields 1-*cyano*-2-*anthraquinonylthiolanthraquinone*, $C_6H_4{:}(CO)_2{:}C_6H_2(CN)\cdot S\cdot C_6H_3{:}(CO)_2{:}C_6H_4$, brownish-yellow, crystalline powder, m. p. above 310°; 2-thiolanthraquinone yields the corresponding *sulphide*, $C_{29}H_{13}O_4NS$, pale yellow needles, m. p. above 310°; and 1:5-dithiolanthraquinone yields 1:5-*di*-1'-*cyanoanthraquinonylthiolanthraquinone*, $C_6H_4{:}(CO)_2{:}C_6H_2(CN)\cdot S\cdot C_6H_3{:}(CO)_2{:}C_6H_3\cdot S\cdot C_6H_2(CN){:}(CO)_2{:}C_6H_4$, yellowish-orange powder, m. p. above 310°. The first and the last of these four compounds produce bluish-green or green vats (alkaline sodium hyposulphite), whilst the other two give brownish-red or yellowish-brown.

Since aromatic mercaptans are difficult to obtain pure, the author replaces them by the corresponding thiocyanates in the preceding reactions. Thus, 1-thiocyanoanthraquinone and 2-bromo-4-cyanoanthraquinone yield the second of the preceding sulphides, whilst phenyl thiocyanate and 2-bromo-1-cyanoanthraquinone yield 1-*cyano*-2-*phenylthiolanthraquinone*, yellow needles, m. p. 207°, which forms a bluish-green vat.

By heating with sulphuric acid (95—97%) at suitable temperatures (100—200°), the preceding sulphides are converted into the corresponding *anthraquinonethioxanthones*. These substances are mostly yellow or brown powders; only those which contain more than one anthraquinone nucleus exhibit the character of pronounced vat dyes.

C. S.

Action of Nitric Acid on Camphane. S. S. Nametkin [with (Mlle.) M. K. Dobrovolskaia and (Mlle.) M. P. Oparina] (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 409—413).—In their unfinished work on the action of nitric acid (D 1·12) on camphane, Konovalov and Kikine (A., 1903, i, 269) obtained a secondary nitro-compound, which, as is shown by the wide limits of its melting point, 125—129°, and of those of the corresponding ketone, 150—165°, and amine, 65—130°, is evidently a mixture. Since, also, the camphane employed in these experiments had m. p. 144—152°, the authors have made a new investigation of this reaction, using pure camphane, prepared by Kishner's method (A., 1911, i, 679). The principal products of the reaction are found to be two stereoisomeric α- and α'-nitrocamphanes, having the structures:


and


Camphane, prepared in 34% yield by heating camphylidenehydrazine in a silver flask at 200—210° with solid potassium hydroxide

and platinised porous tile, has m. p. 157—158°. The camphane was heated with nitric acid (D 1·075) in a sealed tube for thirty hours at 145—150°, the pressure being relieved every ten hours.

α-Nitrocamphane, $C_{10}H_{17}\cdot NO_2$, has m. p. 128—130°, and the isomeric α′-nitrocamphane, m. p. 146—147°, which is almost identical with that of the nitrocamphane obtained by Forster from the corresponding bromonitro-compound (T., 1900, **77**, 251). Both of these nitrocamphanes are non-volatile at the ordinary temperature and resemble camphor in appearance and in their slight odour. Both give Liebermann's reaction and V. Meyer's reaction for secondary nitro-compounds. When oxidised in alkaline solution by means of 2% potassium permanganate solution at 0°, both yield α-camphor (compare Forster, T., 1897, **71**, 1048).

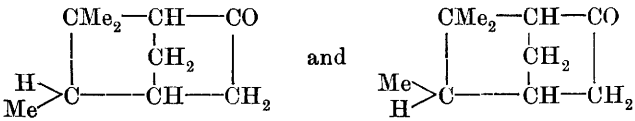
The two nitro-compounds are accompanied by inactive camphoric acid, m. p. 198—200°. T. H. P.

Characteristics of Saturated Bicyclic Hydrocarbons. S. S. Nametkin (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 405—409).—The author gives an account of the general results obtained by treating camphane, camphenilane, and *iso*camphane (see succeeding abstracts) with dilute nitric acid (compare Konovalov, 1893—1906). These three hydrocarbons contain the same bicyclic system and differ only as regards the numbers and positions of the methyl groups present in the molecules. By dilute nitric acid (D 1·075) they are nitrated only at about 140°, this behaviour resembling that of the more stable hydrocarbons of the paraffin series; with acid of this strength, *n*-hexane, for instance, requires a temperature of 140° for its nitration (compare Konovalov, A., 1894, i, 265). In all three cases, the principal nitrogenous product of the reaction is a secondary nitro-compound, no tertiary nitro-derivative being obtained, although each of the hydrocarbons contains at least one tertiary hydrogen atom in the molecule. Since Konovalov's reaction usually yields tertiary nitro-compound in predominating proportion, it is evident that the tertiary hydrogen atom combined with the carbon atom common to the two rings possesses a peculiar character (compare Konovalov, A., 1903, i, 269). Of especial interest is the absence of a tertiary nitro-derivative from the products obtained from *iso*camphane, which contains, in addition, a typical tertiary hydrogen atom united to a carbon atom to which a methyl group is also attached; the tertiary nitro-compound is here replaced by the so-called camphenil nitrite (ω-nitrocamphene), the formation of which indicates the tendency of the hydrocarbon to undergo secondary changes with development of a hemicyclic double linking.

With paraffins or monocyclic hydrocarbons, the nitro-group always enters the molecule in a perfectly definite position, so that only one of the possible secondary nitro-compounds is obtained. With bicyclic hydrocarbons, the general scheme of the reaction is somewhat more complex, the action of the nitric acid being directed to both rings simultaneously. Consequently, wherever possible, as it is with camphenilane, isomerides with nitro-groups in different rings are obtained. Further, there is a marked tendency to form stereo-

isomeric nitro-derivatives, which yield one and the same ketone on oxidation with alkaline permanganate at 0°. The latter reaction is extremely useful in the determination of the structure of nitro-compounds (compare Nametkin and Pozdnjakova, A., 1913, i, 1296). The ketones obtained in this way also occur, in considerable proportion, among the products of the action of nitric acid on the hydrocarbons. Owing to the readiness with which, as a rule, ketones react with nitric acid, they are seldom obtained in more than traces (A., 1909, i, 93, 372; 1910, i, 829), but bicyclic ketones react far less energetically than aliphatic or monocyclic ketones. Similarly, the dibasic acids, also formed by the action of nitric acid on these hydrocarbons, are identical with those obtained by oxidation of the ketones. Confirmation is thus furnished of the connexion between the nitrating and oxidising actions of nitric acid observed repeatedly by Konovalov and by the author. The fact that, in addition to the nitro-compounds, three new bicyclic ketones and two new dibasic acids have been obtained demonstrates the fertility of the application of Konovalov's reaction to bicyclic compounds. T. H. P.

Investigations on *iso*Camphane. S. S. Nametkin and (Mlle.) L. N. Abakumovskaia (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 414—424).—From the results of experiments on mono- and bicyclic hydrocarbons previously made in the author's laboratory, it would be expected that the action of dilute nitric acid on *iso*camphane would yield, in addition to nitro-derivatives, the unknown dibasic *iso*camphocamphoric acid, $\begin{matrix}CMe_2—CH(CO_2H)\\ |\\ CHMe\cdot CH(CO_2H)\end{matrix}>CH_2$, but no trace of this acid could be found. This divergence in behaviour from that of other alicyclic hydrocarbons appears to indicate that the action of the nitric acid is directed, not to the α- or β-position, but to the methylene bridge, but conversion of the mixture of stereoisomeric nitro-compounds obtained into the corresponding ketones by oxidation with alkaline permanganate solution at 0° contradicts this assumption. These ketones, which are termed *iso*camphones, are found to yield the dibasic *iso*camphocamphoric acid on oxidation, such a result being possible only if the carbonyl group of the ketones occupies the α- or β-position. From the results obtained with camphenilane (compare succeeding abstract), which contains the same bicyclic system, it is probable that the nitric acid acts at the β-position, and that the ketones are β- and β′-*iso*camphones having the structures:



The absence of *iso*camphocamphoric acid from the products of the action of nitric acid on *iso*camphane may be due to secondary reactions giving a complex mixture of oxidation products, difficult to separate, derived not only from *iso*camphane, but also from camphene.

In accordance with the results of Konovalov, who found that nitra-

tion of hydrocarbons by means of dilute nitric acid readily yields tertiary nitro-compounds, *iso*camphane gives, in addition to the secondary nitro-compound, the compound described by Jagelki (A., 1899, i, 627) as camphenil nitrite, and shown by Lipp (A., 1913, i, 1077) to be ω-nitrocamphene.

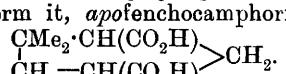
The secondary *nitro*-compound, $C_{10}H_{17}\cdot NO_2$, m. p. 48—49°, forms a yellow, crystalline mass, having the consistency of butter and the characteristic odour of secondary nitro-derivatives of high molecular weight; it gives Liebermann's and V. Meyer's reactions.

β-iso*Camphone*, $C_{10}H_{16}O$, forms a soft, crystalline mass, m. p. 91—92° (wide capillary), and yields a *semicarbazone*, m. p. 196—198°. *β'*-iso-*Camphone* forms a soft, crystalline mass, m. p. 63—64°, b. p. 217—218°/757 mm., and gives a *semicarbazone*, m. p. 195°. Both ketones are highly volatile and have pleasant odours recalling that of camphor.

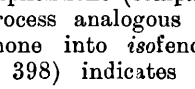
iso*Camphocamphoric acid* (*4 : 4 : 5-trimethylcyclopentane-1 : 2-dicarboxylic acid*), $C_{10}H_{16}O_4$, forms crystalline aggregates or apparently rhombohedral crystals belonging to the monoclinic system.

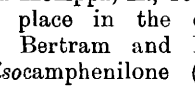
[KARANDÉEV, $a : b : c = 1{\cdot}53 : 1 : 1{\cdot}93$; $\beta = 112°$.] Its alkali, alkaline earth, magnesium, mercuric and manganous salts, like those of camphoric acid, are readily soluble in water; the chromic, ferric, lead, and copper salts of both acids are only slightly soluble, and the silver salt of camphoric acid is appreciably more soluble, and the zinc salt decidedly more soluble, than the corresponding salts of *iso*camphocamphoric acid. T. H. P.

Camphenilane and its Derivatives. S. S. NAMETKIN and (Mlle.) A. M. CHUCHRIKOVAIA (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 425—434. Compare preceding abstracts).—From camphenilone the authors have prepared, by Kishner's method, the new bicyclic hydrocarbon, camphenilane (annexed formula), which yields a secondary nitro-compound, a ketone, and a dibasic acid, $C_9H_{14}O_4$, when treated with dilute nitric acid. A hydrocarbon of the above structure can yield only one acid of this composition, namely, 4 : 4-dimethyl*cyclo*pentane-1 : 3-dicarboxylic acid or, as the authors term it, *apo*fenchocamphoric acid,



Comparison of the ketone obtained with the *iso*camphenilone formed from camphenilone (compare Hintikka and Komppa, A., 1912, i, 278) by a process analogous to that taking place in the conversion of fenchone into *iso*fenchone (compare Bertram and Helle, A., 1900, i, 398) indicates that it is *β-iso*camphenilone (I). The

(I.) 

(II.) 

corresponding secondary nitro-compound would, therefore, be *β*-nitrocamphenilane (II).

Camphenilonehydrazone, $C_9H_{14}{:}N\cdot NH_2$, m. p. 29—31°, b. p.

236—238°/753 mm., obtained by the action of hydrazine hydrate on the ketone in a sealed tube, is accompanied by the corresponding *azine*, $C_9H_{14}{:}N{\cdot}N{:}C_9H_{14}$, which forms colourless prisms, m. p. 148·5°.

Camphenilane, C_9H_{16}, obtained in 70% yield by the action of solid potassium hydroxide on camphenilonehydrazone in presence of platinised porous tile, forms a colourless, crystalline mass, m. p. 15—16°, b. p. 142·5°/753 mm., D_4^{20} 0·8547, n_D^{20} 1·4555. Its nitration was carried out in a sealed tube with nitric acid, D 1·075, at 140—145°. *β-Nitrocamphenilane*, $C_9H_{15}{\cdot}NO_2$, forms crystals, m. p. 18—20°, b. p. 124·5—125°/20 mm., D_4^{20} 1·0770, n_D^{20} 1·4835, and responds to Liebermann's and V. Meyer's reactions. *6-Nitrocamphenilane*, $C_9H_{15}{\cdot}NO_2$, forms crystals, m. p. 89—91°. *β-Camphenilamine*, $C_9H_{15}{\cdot}NH_2$, forms a crystalline mass, m. p. 10—14°, b. p. 189—189·5°/760 mm., D_4^{20} 0·9278, n_D^{20} 1·4822, but was not obtained quite pure, since the melting point of its *benzoyl* derivative, $C_9H_{15}{\cdot}NHBz$, rises from 133—136° after the first, to 141—143° after the third crystallisation.

β-iso-Camphenilone, $C_9H_{14}O$, m. p. 63—65°, b. p. 196·1—196·5°/746 mm., is highly volatile and has a faint odour, recalling that of camphor; its *semicarbazone*, $C_{10}H_{17}ON_3$, has m. p. 192—193°.

4 : 4-Dimethylcyclopentane-1 : 3-dicarboxylic acid (*apofenchocamphoric acid*), $C_9H_{14}O_4$, obtained in almost theoretical yield by oxidising *β-iso*camphenilone with alkaline 4% potassium permanganate solution, forms monoclinic crystals, m. p. 144·5—145°. T. H. P.

Preparation of Santalol Compounds with Sedative Action. J. D. Riedel A.-G. (D.R.-P. 275794).—The biting taste and corrosive action of santalol are not shared by its esters, but the common derivatives of this class have found little application, for they are unstable and possess offensive odours. The esters of some brominated fatty acids have the usual anti-parasitic value of santalol preparations, and, in addition, they are not corrosive, are almost odourless and tasteless, and have very beneficial effects as sedatives and local anæsthetics.

Sandal oil is treated with bromovaleryl bromide or α-bromo-α-ethylbutyryl bromide in pyridine, the product is poured into water and the oily *esters* isolated in the usual way. J. C. W.

Azulene, a Blue Hydrocarbon. II. Alfred E. Sherndal (*J. Amer. Chem. Soc.*, 1915, **37**, 1537—1544).—Azulene (this vol., i, 82) forms a *picrate*, m. p. about 120°, lustrous, black needles, which resembles the corresponding compounds of the aromatic hydrocarbons and affords a means of identifying the hydrocarbon and of effecting its purification. Azulene has now been isolated from the blue fractions of the oils of cubebs and camphor, and also from blue oils prepared from the oils of amyris, guaiacum wood, gurjun, and eucalyptus by the action of a mixture of sulphuric acid and acetic anhydride.

When azulene is submitted to the action of hydrogen in presence of finely divided palladium, it is converted into a faintly green *oil*, $C_{15}H_{26}$, which has D^{25} 0·8935, n_D^{20} 1·490, is optically inactive, and exhibits the characteristics of a tricyclic dihydrosesquiterpene.

The results so far obtained indicate that azulene is tricyclic, and contains an aromatic nucleus, four ethylenic linkings, but no hydroaromatic conjugate double linkings, as it does not suffer reduction when treated with sodium in alcohol; the intense colour of the compound is attributed to a peculiar arrangement of the double linkings. E. G.

Synthetic Caoutchouc from Isoprene. C. HARRIES (*Ber.*, 1915, **48**, 863—868. Compare A., 1914, i, 422).—Steimmig's contention was to the effect that synthetic caoutchouc contained the polymeride of 1 : 6-dimethyl*cyclo*octadiene (A., 1914, i, 307). The author has now shown that carefully purified isoprene (*ibid.*, 817), when heated for six weeks at about 70° in a sealed tube, does not form this polymeride. Special search was made among the products of the decomposition of the ozonide obtained from the artificial caoutchouc for the critical acetonylacetone, but not a trace of its characteristic derivative, 1-anilino-2 : 5-dimethylpyrrole, could be isolated. J. C. W.

Biochemical Synthesis of *d*-Glucosides of Monohydric Alcohols. II. *α*-Alkyl-*d*-glucosides. ÉM. BOURQUELOT (*Ann. Chim.*, 1915, [ix], **3**, 287—337).—A résumé of work already published (compare A., 1913, i, 323, 428, 747, 1008; 1914, i, 144). W. G.

Glucosidification of Glycerol by *β*-Glucosidase (Emulsin). ÉM. BOURQUELOT, M. BRIDEL, and A. AUBRY (*Compt. rend.*, 1915, **160**, 823—825, and *J. Pharm. Chim.*, 1915, [vii], **12**, 33—34. Compare van't Hoff, A., 1911, i, 99; Bayliss, A., 1913, i, 919).—By the action of emulsin on a mixture of dextrose (1 mol.), glycerol (10 mols.), and water (17 mols.) for nine months, followed by suitable treatment to remove the unchanged dextrose and glycerol, the authors have obtained a product in the form of a hard, amorphous mass having $\alpha_D + 27{\cdot}25°$. This product is readily hydrolysed by dilute sulphuric acid or emulsin in aqueous solution, and by measurements of the rotation at definite intervals during the hydrolysis by the latter agent the authors have shown that their product is a mixture of two glyceryl monoglucosides, differing in their rotatory powers and in the readiness with which they are hydrolysed by emulsin. W. G.

Cymarin, the Active Constituent of Apocynum cannabinum. A. WINDAUS and L. HERMANNS (*Ber.*, 1915, **48**, 979—990).—Little is known of the chemical nature of cymarin, the physiologically active constituent of the root of *Apocynum cannabinum*. The substance was extracted with boiling carbon tetrachloride, care being taken during the extraction and subsequent purification to prevent the occurrence of any decomposition. The product crystallises from aqueous methyl alcohol in colourless prisms, $C_{30}H_{44}O_9,MeOH,\frac{1}{4}H_2O$ (m. p. 130—138°, $[\alpha]_D^{20}$ +23·5° in chloroform), the alcohol and water of crystallisation being lost at 95° in a vacuum. The anhydrous compound contains a methoxyl group. The substance also crystallises from aqueous acetone in prisms, which sinter at 120° and melt a

few degrees higher, the analysis in this case indicating a formula $C_{30}H_{46}O_{10},\frac{1}{2}H_2O$.

Cymarin is a glucoside, and when boiled with alcohol containing diluted hydrochloric acid undergoes fission into *cymarose*, $C_7H_{14}O_4$, colourless prisms, m. p. 88°, and *cymarigenin*, $C_{23}H_{30}O_5$. The former substance closely resembles digitoxose in behaviour (Kiliani, A., 1906, i, 66), and from the presence of a methoxyl radicle is in all probability a methyl ether of digitoxose. Cymarigenin appears to be identical in nature with the apocynamarin of Moore (T., 1909, **95**, 734), although this investigator ascribed to it another formula; it crystallises from aqueous methyl alcohol in rhombic tablets, m. p. near 171° (decomp.), which contain water of crystallisation and become completely dehydrated only at 115° in a vacuum. With a solution of a diazonium salt, cymarigenin forms dyes; it reduces ammoniacal silver nitrate solution, forms a *benzoyl* derivative, $C_{30}H_{36}O_7,\frac{1}{2}H_2O$, pearly leaflets, m. p. 230°, and when treated in chloroform solution with hydrogen chloride undergoes conversion into *anhydrocymarigenin*, $C_{23}H_{28}O_4$, rosettes of crystals, m. p. 246° (decomp.). Cymarigenin is a lactone, and although it fails to dissolve in cold sodium carbonate solution does so in warm *N*/10-sodium hydroxide; the solution on acidification, however, does not again give cymarigenin, but an isomeride, *iso-cymarigenin*, which crystallises from diluted acetic acid in pearly leaflets, $C_{23}H_{30}O_5,1\frac{1}{2}H_2O$, m. p. 239°, the water of crystallisation being only partly removed at 85° in a vacuum.

If cymarin is heated with *N*/10-potassium hydroxide solution, only the lactone ring is affected, and on acidification a hydroxy-acid, *cymaric acid*, $C_{30}H_{46}O_{10}$, colourless prisms, m. p. 168°, is obtained; this substance shows little tendency to pass again into a lactone, and when hydrolysed with acids yields *iso*cymarigenin. D. F. T.

The Relationship of Cymarin to Other Heart Poisons of the Vegetable Kingdom. A. Windaus and L. Hermanns (*Ber.*, 1915, **48**, 991—994. Compare preceding abstract).—Attention is drawn to the structural relationship between cymarin and other physiologically active substances of similar origin, such as strophanthin, digitoxin, and antiarin.

Contrary to the statement of Feist (A., 1900, i, 555), strophanthidin, one of the products of the hydrolytic fission of strophanthin, forms a benzoyl derivative, and is indeed identical with cymarigenin. The only difference between the glucosides cymarin and strophanthin lies in the different nature of the sugar constituents of the molecules. The strophanthic acid, $C_{27}H_{38}O_9$, obtained by Feist by the oxidation of strophanthidin with potassium permanganate, is therefore also obtainable from cymarigenin, but the correct formula is $C_{23}H_{30}O_8$; the *dimethyl* ester, needles, m. p. 214°, was prepared by the action of diazomethane on an acetone solution of the acid. D. F. T.

The Preparation of Urinary Indican. Erw. Schwenk and Ad. Jolles (*Biochem. Zeitsch.*, 1915, **69**, 467—470).—Details are given of a method for isolating the indican obtained by treating 1-acetylindoxyl with chlorosulphonic acid in pyridine solution according to the method

already described by the authors (this vol., i, 299). By the modifications here described, the yield of indican can be increased to 76% of the theoretical. S. B. S.

Santonin. XIII. Oxidation of δ-Hydroxysantonin to Santononic Acid. E. WEDEKIND (*Ber.*, 1915, **48**, 891—895).—δ-Hydroxysantonin(*iso*-artemisin) was obtained by the action of sodium acetate or alcoholic potassium hydroxide on chlorosantonin (A., 1905, i, 529). It has been shown that this compound contains the lactone ring and the ketone group of santonin, and the direct proof of the presence of a hydroxyl group is afforded by the action of concentrated hydrochloric acid (future communication). Attempts had been made to oxidise the ketone-alcohol to a diketone, but without much success. It is now found that the substance is readily oxidised by ozone, but that the product is more highly oxidised than was expected. Instead of being the diketone, $C_{15}H_{16}O_4$, it is a ketonic acid, $C_{15}H_{20}O_7$. This is obviously identical with an acid obtained by Angeli and Marino by the oxidation of santonin with alkaline permanganate (A., 1907, i, 321; 1908, i, 543), although these authors could only obtain it as a syrup. A study of the acid will be of importance in connexion with the constitution of santonin.

Santononic acid, $C_{15}H_{20}O_7$, forms colourless crystals, soluble in hot water, decomp. 205°, $[\alpha]_D^{20}$ + 24·03° in alcohol, + 24·49° in chloroform, and yields a bisphenylhydrazone, m. p. 98—100° (*ibid.*). No characteristic salts could be isolated. J. C. W.

Tragacanth. TH. VON FELLENBERG (*Chem. Zentr.*, 1914, ii, 943; from *Mitt. Lebensmittelunters. Hyg.* **5**, 256—259).—Only the insoluble portion of tragacanth, not the gum, contains methoxyl groups. The insoluble portion (bassarin) contains 5·38% of methyl alcohol, calculated on the substance free from cellulose, starch, and ash. Bassorin is less readily hydrolysed than pectin, heating with sodium hydroxide being necessary. The product, *bassoric acid*, is soluble, and can be titrated with sodium hydroxide and phenolphthalein; dilute solutions are precipitated by alcohol and some electrolytes. N. H. J. M.

Physiological Theory of Chlorophyll. D. IVANOVSKI (*Ber. deut. bot. Ges.*, 1914, **32**, 433—447).—The strong absorption of blue rays by chlorophyll (band V), which even exceeds that of the red rays, is mainly due to the yellow pigment; the absorption in this part of the spectrum caused by the photosynthetic pigments is only slight. The energy of the violet rays, which are strongly absorbed by chlorophyllin, is considerably reduced by the yellow pigments. These results account for the protective action of the yellow pigments on the photosynthetically active chlorophyllins.

Judging by the optical properties of their pigments, green leaves are adapted for assimilation in direct sunlight without injury to the chlorophyll. For carbon assimilation the rays of least energy, at the border of the visible spectrum, will be utilised, the red rays being absorbed without hindrance, whilst the violet rays are restrained by the yellow pigments. N. H. J. M.

Function of Chlorophyll. ALFRED J. EWART (*Proc. Roy. Soc.*, 1915, [*B*], **89**, 1—17. Compare Wager, A., 1914, i, 561; Warner, A., 1914, i, 563).—The author has separated the pigments occurring in the green leaf, and has investigated the action of light on them under various conditions.

The separation of the pigments is based on the fact that carotin is only sparingly soluble in cold alcohol, that xanthophyll is soluble in water and in any mixture of alcohol and water, whereas carotin and chlorophyll are precipitated from an alcoholic solution by water, and are readily soluble in light petroleum. Although xanthophyll is soluble in water, contact with the latter will not remove it from a petroleum solution of chlorophyll unless alcohol is also present. The various processes involved in the separation of the pigments are carried out as far as possible out of contact with the air, and in darkness or very feeble light; and the final preparations must also be preserved in the dark until they are needed.

Chlorophyll, xanthophyll, and carotin, when exposed to light in the presence of an abundant supply of oxygen, may act as oxydases, not only to themselves, but also to substances with which they may be in contact, such as hydriodic acid, litmus, or guaiacum. The assumption of the formation of peroxides during the photo-oxidation of these pigments is therefore unnecessary (compare Wager, *loc. cit.*). Chlorophyll and xanthophyll decompose during photo-oxidation into (*a*) solids and (*b*) formaldehyde. The solids consist of colourless, waxy substances and dextro- and lævo-rotatory hexoses. The waxy solids are relatively small in amount in the case of xanthophyll. With dry films of chlorophyll or xanthophyll in dry air free from carbon dioxide, relatively more formaldehyde is produced and less sugar, and the waxy residue weighs much less than the original solid pigment. In moist air more sugar is formed, and the residue weighs almost as much as the original solid. Carotin oxidises more rapidly than xanthophyll or chlorophyll, and yields only a little formaldehyde and a large amount of colourless, waxy solid.

Carbon dioxide combines with chlorophyll, forming xanthophyll and a colourless, waxy solid. The combination only takes place actively in the presence of water, and is accelerated by sunlight. Oxygen is simultaneously evolved and a portion of it may oxidise the xanthophyll, in the presence of sunlight, to formaldehyde, sugar, and the phytyl radicle, which is again built up to form chlorophyll. Neither xanthophyll nor carotin is acted on by moist or dry carbon dioxide.

Xanthophyll is readily converted into carotin by adding magnesium powder or zinc dust to a watery solution of xanthophyll in darkness. In the first case, the reduction is complete in a few hours, whilst with zinc dust it requires two to three days. The reverse change could not be effected through the agency of oxydases.

The results indicate that the assimilation of carbon dioxide is a very complex process, in which chlorophyll and xanthophyll take part, and in which the equilibrium between the products and reacting substances determines the direction in which the reactions take place, whilst light influences this equilibrium and strongly accelerates the tendency to oxidation of the pigments concerned. H. W. B.

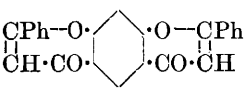
Preparation of 2-Methylcoumaran. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 279864; from *J. Soc. Chem. Ind.*, 1915, **34**, 451).—*o*-Allylphenols, in which the allyl group is directly linked to carbon, are treated with acidic condensing agents, such as hydrogen haloids, and the products are distilled under reduced pressure, when α-methylcoumarans are obtained as colourless liquids. They may be used for pharmaceutical purposes. J. C. W.

Cryoscopic Investigation of Acid Compounds of Dimethylpyrone. V. A. PLOTNIKOV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 730—737).—Cryoscopic investigation in benzene solution of mixtures of dimethylpyrone with trichloro- or tribromo-acetic acid demonstrates the existence in these solutions of complexes of three types, containing: (1) 1 mol. of dimethylpyrone and 1 mol. of the acid; (2) 1 mol. of dimethylpyrone and 2 mols. of acid; (3) 2 mols. of dimethylpyrone and 1 mol. of acid. Complexes of type (1) dissolve almost without decomposition, whilst those of type (2) are partly dissociated into dimethylpyrone and the mono-acidic complex, and those of type (3) undergo marked dissociation in solution. These results are in accord with those previously obtained: (1) by immediate crystallisation (A., 1905, i, 77); (2) by the electrical conductivity method (A., 1906, ii, 144; 1909, ii, 14), and (3) by thermal analysis (A., 1912, i, 792). T. H. P.

Occurrence of Flavone as the Farina of the Primula. HUGO MÜLLER (T., 1915, **107**, 872—878).—The mealy secretion which is found on the leaves, flower stalks, etc., of many species of *Primula* has been identified as almost pure flavone.

After being separated from the plant by brushing or extraction with benzene, and purified, the substance, $C_{15}H_{10}O_2$, formed crystalline tufts, m. p. 99—100°. On hydrolysis with methyl-alcoholic barium hydroxide, it was converted partly into acetophenone, and partly into a *substance*, $C_{15}H_{12}O_3$, yellow prisms, m. p. 120°, which, since it gave acetophenone and salicylic acid on hydrolysis, was identified as *o-hydroxydibenzoylmethane*. Since the original substance is derived from *o*-hydroxydibenzoylmethane by the elimination of water, it seemed probable that it was flavone, and a comparison with synthetic flavone showed complete agreement in properties. G. F. M.

Studies in the Diflavone Group. I. Diflavone. HUGH RYAN and (Miss) PAULINE O'NEILL (*Proc. Roy. Irish Acad.*, 1915, **32**, 48—56).—In view of the wide distribution of the plant dyes of the flavone and flavanol series, none of which, however, have a deeper colour than yellow, and the occurrence of several natural red dyes of unknown constitution, the authors have undertaken the syntheses of substances containing a condensed form of two flavone rings in order to determine the effect of such a structure on the colour of the compounds. The present paper deals with the preparation of a diflavone having the annexed formula.



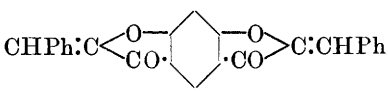
Diacetoresorcinol (4 : 6-diacetyl-1 : 3-dihydroxybenzene), prepared from resorcinol diacetate according to the method described by Eykman, Bergema

and Henrard (*Chem. Weekblad*, I, 453), is converted by the action of methyl sulphate and aqueous potassium hydroxide into the dimethyl ether, m. p. 171°, which readily condenses with benzaldehyde in alcoholic solution in the presence of sodium hydroxide, yielding *di-o-hydroxydichalkone dimethyl ether* [4 : 6-*dicinnamoyl*-1 : 3-*dimethoxybenzene*], $C_6H_2(OMe)_2(CO{\cdot}CH{:}CHPh)_2$. This crystallises in light yellow prisms, m. p. 156—157°, gives an orange coloration with sulphuric acid, and forms a *tetrabromide*, almost colourless prisms, m. p. 185—186° (decomp.). When heated with anhydrous aluminium chloride in xylene solution it undergoes demethylation with the formation of *di-o-hydroxydichalkone* [4 : 6-*dicinnamoyl*-1 : 3-*dihydroxybenzene*], $C_6H_2(OH)_2(CO{\cdot}CH{:}CHPh)_2$, which separates from benzene in small, doubly refractive, light yellow crystals of cubic appearance, m. p. 196—198°, gives a red coloration with ferric chloride, and is also obtained in small yield by shaking a solution of 4 : 6-diacetyl-1 : 3-dihydroxybenzene in very dilute sodium hydroxide with benzaldehyde for several weeks.

Dihydroxydichalkone diacetate tetrabromide [4 : 5-*di-αβ-dibromo-β-phenylpropionyl*-1 : 3-*diacetoxybenzene*],

$$C_6H_2(OAc)_2(CO{\cdot}CHBr{\cdot}CHPhBr)_2,$$

prepared by heating the preceding 4 : 6-dicinnamoyl-1 : 3-dihydroxybenzene with acetic anhydride and sodium acetate and treating the resulting oily *diacetyl* derivative with bromine in chloroform solution, crystallises in colourless needles, m. p. 176—178°, and is converted by warming with alcoholic potassium hydroxide into diflavone. The diflavone thus formed is contaminated with a small amount of *dibenzylidenedicoumarone* (annexed formula), the presence of which was indicated by the development of an orange coloration with sulphuric acid.



A purer preparation was obtained as follows : 4 : 6-diacetyl-1 : 3-dimethoxybenzene is condensed with methyl benzoate by means of metallic sodium at 120°, and the resulting *dibenzoylacetoresorcinol dimethyl ether* [4 : 6-*dibenzoylacetyl*-1 : 3-*dimethoxybenzene*],

$$C_6H_2(OMe)_2(CO{\cdot}CH_2Bz)_2,$$

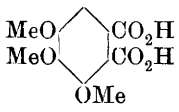
light yellow plates, m. p. 200—201°, heated for five hours at 135° with hydriodic acid (D 1·7).

Diflavone crystallises in faint yellow needles, softens at 275°, melts at 281—282° to a brown liquid, and yields yellow solutions in sulphuric acid having a magnificent blue fluorescence.

6-*Benzoylacetyl*-7-*methoxyflavone* (6-*benzoylacetyl*-7-*methoxy*-2-*phenyl*-γ-*benzopyrone*), $CH_2Bz{\cdot}CO{\cdot}C_6H_2(OMe)<^{O—CPh}_{CO{\cdot}CH}$, prepared by heating 4 : 6-dibenzoylacetyl-1 : 3-dimethoxybenzene with hydriodic acid (D 1·7) at 135° for only one hour, crystallises in faint yellow prisms, m. p. 238°; its solutions in sulphuric acid show a green fluorescence. F. B.

Colchicine. III. A. Windaus and L. Krellwitz (*Chem. Zentr.*, 1914, ii, 1455—1456).—Further experiments on the degradation of colchicine are described.

I. The trimethoxy-*o*-phthalic acid obtained by oxidising colchicine with hot potassium permanganate solution must have the annexed formula (compare Windaus, A., 1911, i, 904; Voswinckel and de Weerth, A., 1912, i, 472; Bargellini and Molina, *ibid.*, 773), since it is converted into gallic acid by boiling hydriodic acid.



II. Colchicinic acid is oxidised by potassium permanganate to succinic and oxalic acids; similar products, and small quantities of picric acid, are obtained from colchicine and nitric acid. III. When fused with potassium hydroxide and subsequently oxidised with hot permanganate solution, colchicine gives terephthalic and trimellitic acids; colchicinic acid gives these products when fused with alkali. Apparently, therefore, in addition to the pyrogallol ring a second ring is present in colchicine, which is degraded in an oxidising alkali fusion to terephthalic and trimellitic acids.

IV. When a well-cooled solution of colchiceine in dilute sodium hydroxide is treated with iodine dissolved in aqueous potassium iodide, substitution and oxidation occur simultaneously with the formation of a *substance*, $C_{20}H_{22}O_5NI$, yellow prisms, m. p. 228—230°. The reaction appears to proceed according to the equation: $C_{21}H_{23}O_6N + 4I + 5NaOH = C_{20}H_{22}O_5NI + 3NaI + Na_2CO_3 + 3H_2O$. The new substance does not give the ferric chloride reaction of colchiceine, nor is the reaction obtained when the iodine atom is replaced by hydrogen. It is very slightly soluble in dilute sodium carbonate solution, soluble in cold alkali hydroxide, and re-precipitated when the solution is boiled. Boiling potassium hydroxide solution does not cause removal of the iodine atom, which, however, is readily replaced under the action of zinc dust and boiling glacial acetic acid; the *product*, $C_{20}H_{23}O_5N$, forms white needles, m. p. 150°, which contain water of crystallisation; the anhydrous substance melts above 200°. It does not give a coloration with ferric chloride. When boiled with alcoholic hydrogen chloride, it loses acetic acid and yields a *hydrochloride*, $C_{18}H_{21}O_4N,HCl$, leaflets, m. p. 241° after softening above 200°. The compound, $C_{20}H_{22}O_5NI$, gives an *acetyl* derivative, $C_{22}H_{24}O_6NI$, m. p. about 144—145°.

H. W.

Preparation of a Hydro-derivative of Colchicine. F. Hoffmann-La Roche & Co. (D.R.-P. 279999; from *J. Soc. Chem. Ind.*, 1915, **34**, 452).—Colchicine is reduced by hydrogen in the presence of finely divided or colloidal palladium. The product is probably tetrahydrocolchicine, and is not so toxic as colchicine. J. C. W.

Preparation of Hydrastinine Derivatives. E. Merck (D.R.-P. 279194; from *J. Soc. Chem. Ind.*, 1915, **34**, 451).—Homopiperonylamine derivatives of the type $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CHAlk{\cdot}NR{\cdot}CHO$, where R = hydrogen, alkyl or arylalkyl, are condensed by such agents as phosphoric oxide or the pentachloride, or aluminium or zinc chloride, to dihydro*iso*quinoline (hydrastinine) bases. When R = hydrogen, the 6 : 7-methylenedioxy-3-alkyl-3 : 4-dihydro*iso*quinolines obtained are subsequently converted into *N*-alkyl (or arylalkyl) derivatives. J. C. W.

Preparation of Hydrohydrastinine and its Homologues. E. MERCK (D.R.-P. 280502; from *J. Soc. Chem. Ind.*, 1915, **34**, 636).—*N*-Acetonylhomopiperonylamine or an alkyl derivative of the general formula, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CHR''{\cdot}NR'{\cdot}CH_2{\cdot}COMe$, where R' and R'' = hydrogen or alkyl, loses methyl alcohol when treated with a condensing agent like phosphoric oxide, and forms an *iso*quinoline derivative. Hydrohydrastinine is obtained from *N*-acetonylhomopiperonylamine, and the homologues from *N*-ethyl-*N*-acetonylhomopiperonylamine and such compounds. J. C. W.

Appearance of Polymorphic Forms of Narcotine and Codeine. ROBERT KREMANN and NORBERT SCHNIDERSCHITZ (*Monatsh.*, 1914, **35**, 1423—1426).—Gaubert (A., 1913, i, 643) has shown that codeine exists in five crystalline forms with transition points at 60°, 40°, and two between 45° and 60°. Narcotine exists in two stable crystalline forms with a transition point between 50° and 80°. The authors have examined the time-cooling curves of these substances and find inflexion points at 147° and 149° respectively, but fail absolutely to find any in the regions indicated by Gaubert. This does not, however, indicate that the crystal forms obtained by Gaubert do not exist. The authors advance several explanations for the absence of the inflexion points, the most probable being that the rate of transition from one form to another is so slow that the change has not taken place during the experiments quoted, which lasted about 120 minutes. J. F. S.

Channa, a Delicacy of the Hottentots (Mesembrianthemum expansum, L., and M. tortuosum, L.). C. HARTWICH and E. ZWICKY (*Chem. Zentr.*, 1915, i, 95—96; from *Apoth.-Zeit.*, 1914, **29**, 925, 937, 949, 961).—A short account is given of the history, occurrence, composition, and properties of the substance.

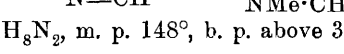
Crystalline deposits containing magnesium and citric and phosphoric acids are found in the mesophyll of the dried leaves. The active constituent of the drug is the alkaloid *mesembrine*, $C_{16}H_{19}O_4N$, obtained by percolation of the powdered drug with 1% hydrochloric acid and purified by solution in anhydrous ether and precipitation with hydrogen chloride. The alkaloid is freely soluble in chloroform, alcohol or acetone, sparingly in ether, water or alkalis, very sparingly in light petroleum or benzene. With vanadic sulphuric acid it gives a brownish-red solution, the green tint of which becomes more pronounced on warming, and which after twenty-four hours becomes bright green. Mesembrine behaves as a phenol, and is unsaturated. The leaves contain as a maximum 0·3%, the stems and roots 0·86% of the alkaloid. According to Cloetta, mesembrine has an action somewhat resembling, but distinct from, that of cocaine. In all branches of the family of *Mesembrianthemum* species are found which do and do not contain the alkaloid.

The wax of the channa, which is soluble in hot alcohol, contains 25% of saponifiable material. The unsaponifiable portion consists of a mixture of *mesembrene*, $C_{28}H_{56}$, colourless, rhombic plates, m. p. 68—69°, and *mesembrol*, $C_{31}H_{64}O$ or $C_{30}H_{62}O$, crystals, m. p. 73—74°.

Mesembrene when boiled with acetic anhydride and sodium acetate combines with acetic acid (1 mol.), yielding the *substance*, $C_{30}H_{60}O_2$, m. p. 66—67°. The wax is found in the epidermis of the leaves and, probably, of the stalks. H. W.

Preparation of Alkyloxymethyl Ethers of Morphine. C. MANNICH (D.R.-P. 280972; from *J. Soc. Chem. Ind.*, 1915, **34**, 452).—The alkali salts of morphine are treated with ethers of the type $Hal.CH_2{\cdot}O{\cdot}Alk$. The methoxymethyl ether of morphine is more active than the alkyl ethers, but less active than the free alkaloid. It is readily converted into *N*- or *O*-alkyl derivatives. The methoxymethyl group is removed on heating the compounds with sulphurous acid. J. C. W.

Alkaloids of Tobacco Extract. EUGEN NOGA (*Chem. Zentr.*, 1915, i, 434; from *Fachliche Mitt. öst. Tabakregie*, 1914).—The material was obtained by systematic extraction of residues from Turkish tobacco with water and evaporation of the extract in a vacuum. By the use of benzene, a small quantity of alkaloid, which was not volatile with steam, was obtained from this extract, and was separated by distillation into four fractions. I. *Nicotoine*, $C_8H_{11}N$, colourless, mobile liquid with a peculiar intense odour resembling that of pyridine, b. p 208°; D_4^{21} 0·9545, n_D^{20} 1·5105. It gives the usual alkaloidal reactions. With hydrochloric, sulphuric and picric acids, mercuric and platinic chlorides, it yields, in part, well-crystallised *salts* of definite m. p. II. Nicoteine (compare Pictet and Rotschy, A., 1901, i, 339). III. iso*Nicoteine*, $C_{10}H_{12}N_2$, colourless, viscous, oily liquid, with a rather powerful, very persistent odour. It is optically inactive, and has b. p. 293° (darkening), D_4^{20} 1·0984, n_D^{20} 1·5749. With hydrochloric, sulphuric and picric acids, mercuric, platinic and auric chlorides it yields, in part, well-crystallised *salts*. It forms a *methiodide*. It is converted by oxidation into nicotinic acid, gives the pine-shaving reaction, immediately decolorises potassium permanganate, and, therefore, obviously has the formula



IV. Nicotelline, $C_{10}H_8N_2$, m. p. 148°, b. p. above 300° (*loc. cit.*). H. W.

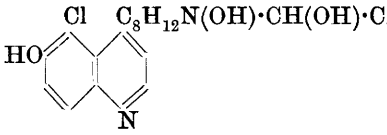
Action of Chlorine on Quinine. A. CHRISTENSEN (*Ber. Deut. pharm. Ges.*, 1915, **25**, 256—281).—When a solution of quinine hydrochloride in a mixture of acetic and hydrochloric acids is treated with chlorine (1 mol.) there is produced an additive compound, *quinine dichloride*, $C_{20}H_{24}O_2N_2Cl_2$, a colourless, amorphous powder, m. p. 97°, which dissolves in dilute oxy-acids giving solutions with a blue fluorescence; the base is diacid, and forms a *dihydrochloride*, prisms with $2H_2O$, sparingly soluble *nitrate*, hexagonal prisms, *dihydrobromide perbromide*, $C_{20}H_{24}O_2N_2Cl_2,2HBr,Br_2$, orange-red, crystalline powder, and *iodosulphate*, $4C_{20}H_{24}O_2N_2Cl_2,3H_2SO_4,2HI,I_4,7$ or 8 H_2O, which closely resembles the corresponding derivative of quinine. Under energetic treatment with alcoholic potassium hydroxide the new base eliminates two molecules of hydrogen chloride, yielding dehydroquinine, $C_{20}H_{22}O_2N_2$, m. p. 181°.

If quinine hydrochloride is treated in solution in cold dilute hydrochloric acid with chlorine (1 mol.) dissolved in water, the product is an additive *compound* of quinine and hypochlorous acid,

$$C_{20}H_{24}O_2N_2Cl\cdot OH,$$

to which the name *quinine hydroxychloride* is given; this is an amorphous, colourless powder, m. p. 110°, which can be isolated as the *nitrate* by the addition of ammonium nitrate solution.

Chlorine (2 mols.) in aqueous solution acts on a cold solution of quinine hydrochloride in dilute hydrochloric acid, giving a *base*, $C_{19}H_{22}O_3N_2Cl_2$, which separates as the dihydrochloride on the addition of sodium chloride. The new base, for which the annexed structure is suggested, forms colourless needles with $4H_2O$, m. p. 172—173°; it contains three hydroxyl groups, and forms a *triacetyl* derivative and a *dibenzoyl* derivative; when oxidised with nitric acid it gives pyridine-2 : 3-dicarboxylic acid. The suggested structure receives confirmation from the formation of a *base*,



$$C_{19}H_{22}O_2N_2Cl_2,4H_2O$$

(*dihydrochloride*, yellow prisms with $3H_2O$; *nitrate*, crystalline), when chlorine water is allowed to act on hydrochloroquinine, $C_{20}H_{25}O_2N_2Cl$; the last-named substance does not contain any aliphatic ethylenic linking, so that the new chlorine atom in the product must have entered the quinoline nucleus, which fact leads to the probable conclusion that one hydroxyl group in the base, $C_{19}H_{22}O_3N_2Cl_2$, must have been produced at the terminal ethylenic linking of the side-chain in quinine, whilst another hydroxyl group marks the previous position of the methoxyl radicle. Further confirmation of the structure is supplied by the conversion of 6-methoxyquinoline into 5-chloro-6-hydroxyquinoline under the action of chlorine water in hydrochloric acid solution.

The product of the action of chlorine (3 mol.) on a solution of quinine hydrochloride in dilute hydrochloric acid is an unstable *base*, $C_{19}H_{21}O_3N_2Cl_3$, which can be separated from solution as the *nitrate*, colourless, hexagonal leaflets, whilst the action of chlorine on hydrochloroquinine produces an analogous *compound*, $C_{19}H_{21}O_2N_2Cl_3$ (*nitrate*, almost quadratic tablets), the difference between these two bases being the replacement of the hydroxyl group in the side-chain of the former by hydrogen in the latter. Both these bases give a green coloration with aqueous ammonia, and also liberate iodine from potassium iodide; it is therefore probable that each contains the grouping $-CO\cdot CCl_2-$ in the quinoline nucleus.

Quinine dichloride (described above) also reacts with chlorine (2 mol.), yielding a *base*, $C_{19}H_{20}O_2N_2Cl_4$, which is separated as the crystalline *nitrate*; this contains one active chlorine atom capable of displacing iodine from potassium iodide and so probably contains the grouping $-CO\cdot CCl_2-$, which is also present in the products $C_{19}H_{21}O_3N_2Cl_3$ and $C_{19}H_{21}O_2N_2Cl_3$, obtained from quinine and hydrochloroquinine respectively. It is noteworthy that, although only one chlorine atom is

reactive in these compounds, they liberate two equivalents of iodine from potassium iodide, the grouping $-CO\cdot CCl_2-$ undergoing conversion into $-C(OH):CCl-$. D. F. T.

Strychnos Alkaloids. XXIII. Oxalic Acid and an Amino-acid, $C_{17}H_{18}O_4N_2$, as Fission Products of Strychninolonic Acid-*a*. HERMANN LEUCHS and GEORG SCHWAEBEL (*Ber.*, 1915, **48**, 1009—1015).—Acetylstrychninolonic acid-*a* (Leuchs and Schwaebel, A., 1914, i, 861), judging by analogy with the dibasic acid obtained from acetylbrucinolone-*a* (Leuchs and Rauch, A., 1914, i, 317), may be a half amide of oxalic acid and an amino-acid, and experiment confirms this idea.

When the barium salt is heated with hydrobromic acid (D 1·47) on the water-bath, oxalic acid is produced together with a *substance*, which, after treatment with methyl alcohol and hydrobromic acid, is obtained as a crystalline *solid*, $C_{18}H_{20}O_4N_2,2HBr$; this sinters at 225° and gradually decomposes on further heating. This substance is stable only in presence of free hydrobromic acid, and further treatment with methyl or ethyl alcohol converts it into a *monohydrobromide*, $C_{18}H_{20}O_4N_2,HBr$, rectangular, pale green prisms, m. p. 258—260° (decomp.). The formulæ of these two compounds suggest that in the treatment of the original product of the reaction with hydrobromic acid, the methyl alcohol has caused esterification with formation of a methyl ester; this supposition is confirmed by the action of barium hydroxide solution on the dihydrobromide, yielding needles of a *barium* salt, $(C_{17}H_{17}O_4N_2)_2Ba$, whilst both hydrobromides are converted by aqueous ammonia solution into an acid *amide*, $C_{17}H_{18}O_4N_2$, needles or prisms, m. p. near 280° (decomp.), which under the action of nitric acid passes into a *nitrate*, $C_{17}H_{19}O_3N_3,HNO_3$, octahedra or prisms.

If the original barium salt of acetylstrychninolonic acid-*a* is heated with hydrochloric acid in a similar manner to that described for hydrobromic acid, the product does not undergo esterification on treatment with methyl alcohol, but consists of the *hydrochloride* of an amino-acid, $C_{17}H_{18}O_4N_2,HCl$, hexagonal columns, decomp. near 278°; which reacts with phenylcarbimide in the presence of dilute alkali yielding an amorphous carbamido-*acid*. The corresponding *sulphate*, $C_{17}H_{18}O_4N_2,H_2SO_4$, tetragonal or hexagonal leaflets, was obtained by evaporating the hydrobromic acid product with sulphuric acid under reduced pressure. The sulphate and hydrochloride do not give any amide with ammonia, but are converted by successive treatment with hydrobromic acid and methyl alcohol into the dihydrobromide, $C_{18}H_{20}O_4N_2,2HBr$, already described.

From the facts that the barium salt, $(C_{17}H_{17}O_4N_2)_2Ba$, is neutral in reaction, and that it cannot be obtained directly from the sulphate and hydrochloride just described, the conclusion is drawn that it is not derived from the same amino-acid as these salts, but from an isomeride the occurrence of which is to be attributed to intramolecular change. D. F. T.

Spontaneous Oxidations in Presence of Aldehydes. Derivatives of Benzylidenemethyl*iso*-oxazolone. MARIO BETTI and LUIGI ALESSANDRI (*Gazzetta*, 1915, **45**, i, 462—469).—It has been pre-

viously shown (*ibid.*, 362) that, when dissolved in ammoniacal alcohol containing a little benzaldehyde, 4-benzylidene-3-phenyl*iso*-oxazolone is converted into the amide of 3 : 5-diphenyl*iso*-oxazole-4-carboxylic acid, the presence of the aldehyde favouring the action of atmospheric oxygen. It is now found that, under similar conditions, 4-benzylidene-3-methyl*iso*-oxazolone undergoes an analogous oxidation, yielding the amide of 5-phenyl-3-methyl*iso*-oxazole-4-carboxylic acid, which can be converted into the free acid, and this, by heating, into 5-phenyl-3-methyl*iso*-oxazole (compare Goldschmidt, A., 1895, i, 529; Moureu and Brachin, A., 1904, i, 95).

In this case, also, phenylmethyl*iso*-oxazolecarboxylic acid may be prepared in another way, namely, by the action of hydroxylamine on ethyl benzoylacetoacetate, but the acid thus obtained is isomeric with 5-phenyl-3-methyl*iso*-oxazole-4-carboxylic acid, and must be regarded as 3-phenyl-5-methyl*iso*-oxazole-4-carboxylic acid. This conclusion is, however, not quite satisfactory, since, when carbon dioxide is eliminated by heating, these two acids yield derivatives of *iso*-oxazole which appear to be identical; interchange of the phenyl and methyl groups as a result of heating is, however, improbable. Further experiments are in progress with the view of explaining the isomerism of these two acids.

5-*Phenyl*-3-*methyl*iso-*oxazole*-4-*carboxylic acid*, $O<\begin{matrix}CPh:C\cdot CO_2H\\ |\\ N=\!=CMe\end{matrix}$, forms red or straw-yellow, crystalline flocks, m. p. 157°, decomp. about 220°; the *calcium* salt ($+3H_2O$) was analysed. The corresponding *amide*, $C_{11}H_{10}O_2N_2$, forms faint red, flattened needles, m. p. 256—257°, and has the normal molecular weight in boiling alcohol.

3-*Phenyl*-5-*methyl*iso-*oxazole*-4-*carboxylic acid*, (?), $C_{11}H_9O_3N$, forms massive, colourless prisms, m. p. 189°, and its *ethyl* ester, $C_{13}H_{13}O_3N$, colourless, prismatic crystals, m. p. 52—53°. T. H. P.

Hæmocyanin. Ernst Philippi (*Chem. Zentr.*, 1914, ii, 1165).—A substance, containing about 10% of copper, is obtained from the blood of *Helix pomatia*; even with very small quantities, it yields an intense pyrrole reaction with a pine-shaving. The author is led to the conclusion that the copper in hæmocyanin is united to a complex containing pyrrole. H. W.

Preparation of Pyrrolidine Derivatives. Chemische Fabrik auf Aktien (vorm. E. Schering) (D.R.-P. 280971).—Some new pyrrolidine derivatives may be obtained by condensing acylpyruvic esters with benzaldehyde and ortho-substituted anilines, or with substituted benzaldehydes and anilines, or with benzaldehyde and heterocyclic compounds, or with heterocyclic aldehydes and amines, in non-alcoholic solution.

Benzaldehyde, *o*-toluidine, and acetylpyruvic ester in ether yield 4 : 5-*diketo*-3-*acetyl*-2-*phenyl*-1-*o*-*tolylpyrrolidine*, pink crystals, m. p. 177—179°; anisidine, benzaldehyde, and acetylpyruvic ester in toluene yield 4 : 5-*diketo*-3-*acetyl*-2-*phenyl*-1-*o*-*methoxyphenylpyrrolidine*, m. p. 225—227° (decomp.); aniline, piperonaldehyde, and acetylpyruvic ester in boiling benzene give 4 : 5-*diketo*-3-*acetyl*-2-*piperonyl*-1-*phenylpyr-*

rolidine, m. p. 197°; *p*-toluidine, *p*-dimethylaminobenzaldehyde, and acetylpyruvic ester in benzene yield 4 : 5-*diketo*-3-*acetyl*-2-p-*dimethylaminophenyl*-1-p-*tolylpyrrolidine*, $NMe_2 \cdot C_6H_4 \cdot CH<\begin{matrix}CHAc\text{——}CO\\ |\quad\quad\ |\\ N(C_6H_4Me)\cdot CO\end{matrix}$, as a brown powder, m. p. 166° (decomp.); benzaldehyde, 8-aminoquinoline, and acetylpyruvic ester in boiling benzene form 4 : 5-*diketo*-3-*acetyl*-1-*quinolyl*-2-*phenylpyrrolidine*, $C_9NH_6 \cdot N<\begin{matrix}CHPh\cdot CHAc\\ |\quad\quad\ |\\ CO\text{——}CO\end{matrix}$, m. p. 222° (decomp.); 4-amino-1-phenyl-2 : 3-dimethylpyrazolone, benzaldehyde, and acetylpyruvic ester in benzene at 100—110° yield 4 : 5-*diketo*-3-*acetyl*-2-*phenyl*-1(1′-*phenyl*-2′ : 3′-*dimethylpyrazolonyl*)*pyrrolidine*,

$$NPh<\begin{matrix}CO\text{---}C\text{-}N<\begin{matrix}CO\text{---}CO\\ |\quad\quad\ |\\ CHPh\cdot CHAc'\end{matrix}\\ NMe\cdot CMe\end{matrix}$$

as a pale brown powder with a bitter taste; furfuraldehyde, aniline, and acetylpyruvic acid in benzene give 4 : 5-*diketo*-3-*acetyl*-1-*phenyl*-2-*furylpyrrolidine* in yellowish-green crystals, m. p. 190° (decomp.); and benzoylpyruvic ester, benzaldehyde, and *o*-anisidine in benzene yield 4 : 5-*diketo*-3-*benzoyl*-2-*phenyl*-1-*o*-*methoxyphenylpyrrolidine*,

$$OMe\cdot C_6H_4\cdot N<\begin{matrix}CHPh\cdot CHBz\\ |\quad\quad\ |\\ CO\text{---}CO\end{matrix},$$

m. p. 215—217° (decomp.).

These new compounds have pronounced diuretic properties.

J. C. W.

Electrical Conductivity of the Amines and Dicarboxylic Acids of Pyridine. Hans Tropsch (*Monatsh.*, 1914, **35**, 775—779).—The electrical conductivity of a number of mono- and di-amines, and dicarboxylic acids of pyridine have been determined at 25°. The dissociation constant has been calculated in each case with the object of showing the relative strengths of the various acids and bases. The values for k in the cases examined are: 2-aminopyridine, $1{\cdot}4 \times 10^{-7}$; 3-aminopyridine, $3{\cdot}9 \times 10^{-8}$; 4-aminopyridine, $1{\cdot}3 \times 10^{-5}$; 2 : 6-diaminopyridine, $6{\cdot}4 \times 10^{-8}$; 3 : 5-diaminopyridine, $1{\cdot}0 \times 10^{-7}$; 2 : 4-diaminopyridine, $1{\cdot}3 \times 10^{-5}$; pyridine-2 : 6-dicarboxylic acid, $6{\cdot}2 \times 10^{-3}$, and pyridine-2 : 4-dicarboxylic acid, $7{\cdot}0 \times 10^{-3}$. It will thus be seen that the presence of an amino-group or a carboxyl group in position 4 gives a stronger acid or base than when these groups are in positions 2 or 3.

J. F. S.

Sulphonation of Pyridine Bases. Hans Meyer and Wolfgang Ritter (*Monatsh.*, 1914, **35**, 765—774).—The sulphonation of pyridine may be readily accomplished by boiling with sulphuric acid in the presence of vanadyl sulphate. If the pyridine is impure, poor yields are obtained. Prolonged heating also diminishes the yield, part of the sulphonic acid being completely destroyed by the vanadyl sulphate and part reconverted into pyridine.

The influence of various metallic sulphates on the sulphonation of pyridine has been investigated by Weidel and Murmann (A., 1896, i, 104), who found that, after heating for sixty hours, aluminium sulphate gave an increased yield of the sulphonic acid, whilst ferric sulphate con-

siderably diminished the yield; zinc, ammonium, magnesium, chromium and the alkali sulphates were without action. By reducing the period of heating the authors show that, with the exception of ferric sulphate, none of these metallic salts exercise a catalytic action on the formation of the sulphonic acid, the increased yield, in the case of aluminium sulphate, being due to the fact that this salt exerts no decomposing effect on the sulphonic acid formed in the reaction. Ferric sulphate, on the other hand, acts as a catalyst during the sulphonation, but at the same time decomposes the sulphonic acid, the latter effect becoming more pronounced when the period of heating is prolonged.

α-Picolinesulphonic acid, prepared by sulphonating picoline in the presence of vanadyl sulphate and purified by means of its *ammonium* and *barium* salts, forms colourless crystals. F. B.

Some Tetrahydropyridines and their Behaviour with Aldehydes. A. LIPP and E. WIDNMANN (*Annalen*, 1915, **409**, 79—147).—Very largely a repetition of work already published (Lipp, A., 1882, 218; 1892, 1243; 1896, i, 317; 1905, i, 610, 662). Since the course of the reaction between formaldehyde and 1 : 2-dimethyl-Δ^2-tetrahydropyridine has been differently interpreted by Lipp (*loc. cit.*) and Ladenburg (A., 1899, i, 303), the authors have re-investigated the reaction and found that the constitution of the product is different from those ascribed to it by the preceding investigators. In the first place there can be no doubt that the product is a 3-derivative of piperidine (not a 2-derivative, as stated by Ladenburg [A., 1898, i, 687]), because when it is successively reduced by sodium and alcohol, dehydrated by concentrated hydrochloric acid, and reduced by tin and hydrochloric acid, it yields 1-methyl-3-ethylpiperidine, the identity of which is established by direct comparison. There is a good deal of evidence for the view that 1 : 2-dimethyl-Δ^2-tetrahydropyridine exists in aqueous solution as methyl δ-methylaminobutyl ketone. Assuming this to be so, the reaction with formaldehyde may be represented by the scheme:

$$NMe\langle\begin{matrix}CH_2\cdot CH_2\\ CMe{=}CH\end{matrix}\rangle CH_2 \xrightarrow{H_2O} NHMe\cdot[CH_2]_4\cdot COMe \xrightarrow{CH_2O}$$

$$NHMe\cdot[CH_2]_3\cdot CHAc\cdot CH_2\cdot OH \xrightarrow{H_2O} NMe\langle\begin{matrix}CH_2-CH_2\\ CH_2\cdot CHAc\end{matrix}\rangle CH_2,$$

according to which the product is 3-acetyl-1-methylpiperidine, and its whole behaviour accords well with this formula.

In a similar manner, the course of the reaction of 1 : 2-dimethyl-Δ^2-tetrahydropyridine with other aliphatic aldehydes can be explained. The great majority of the compounds mentioned, which are fully described, are not new, but are the old compounds of Lipp and of Ladenburg described under the new names corresponding with the new constitutions ascribed by the authors to the products of the reaction between aldehydes and homologues of tetrahydropyridine. The following appear to be new: 3-Acetyl-1 : 2-dimethylpiperidine and hydroxylamine hydrochloride react in aqueous solution to form the *hydrochloride*, m. p. 191—193° (decomp.), of the *oxime*,

$$NOH{:}CMe\cdot CH\langle\begin{matrix}CH_2---CH_2\\ CHMe\cdot NMe\end{matrix}\rangle CH_2,$$

prisms, m. p. 129—131°; the corresponding *semicarbazone*, $C_{10}H_{20}ON_4$, has m. p. 168—170° (decomp.). 2-Methyl-1-ethyl-Δ^2-tetrahydropyridine (*picrate*, $C_8H_{15}N,C_6H_3O_7N_3$, prisms, m. p. 126°), existing in aqueous solution as methyl δ-ethylaminobutyl ketone, yields the *benzoyl* derivative, $NEtBz\cdot[CH_2]_4\cdot COMe$, monoclinic prisms, m. p. 56—57°, *oxime*, $NOH{:}CMe\cdot[CH_2]_4\cdot NHEt$, m. p. 96—97°, and semicarbazone (as the *hydrochloride*, $C_9H_{20}ON_4,HCl$, m. p. 166—168° [decomp.]) of this ketone by the usual methods.

3-Acetyl-1-ethylpiperidine forms in the normal manner an *oxime*, $C_9H_{18}ON_2$, m. p. 128—129°, prisms, *semicarbazone*, m. p. 160° (decomp.), and phenylhydrazone (as the *hydrochloride*, yellow crystals, m. p. 217—218° [decomp.]).

1 : 3-*Diethylpiperidine*, b. p. 177—185°/726 mm., prepared by reducing 1-ethyl-3-vinylpiperidine by tin and hydrochloric acid, is a colourless, mobile liquid, and forms a *hydrochloride*, $C_9H_{19}N,HCl$, prisms, m. p. 186—188°, and crystalline *aurichloride*.

3-Acetyl-2-methyl-1-ethylpiperidine forms a platinichloride, m. p. 187° (decomp.) (Ladenburg gives 167°), *mercurichloride*,

$$C_{10}H_{19}ON,HCl,6HgCl_2,$$

m. p. about 200° (decomp.), softening at 140°, *oxime* (*platinichloride*, m. p. 185° [decomp.], yellow, crystalline powder), and *semicarbazone*, m. p. 184—186° (*platinichloride*, decomp. about 150°).

2 : 3-Dimethyl-Δ^2-tetrahydropyridine, like other tetrahydropyridines containing a methyl group in position 2, exists in aqueous solution as the corresponding amino-ketone, methyl δ-amino-α-methylbutyl ketone, $NH_2\cdot[CH_2]_3\cdot CHMeAc$, and yields the *benzoyl* derivative, almost colourless, viscous oil (*oxime*, $C_{14}H_{20}O_2N_2$, prisms and plates, m. p. 117—118°), and *oxime*, an oil, of this by the usual methods. By prolonged heating with tin and hydrochloric acid it is reduced to 2 : 3-*dimethylpiperidine*, b. p. 138—140°/720 mm., a clear, mobile liquid having a pronounced odour of piperidine, which forms a *hydrochloride*, needles, *platinichloride*, m. p. 145° (decomp.), *aurichloride*, m. p. 130—135°, *mercurichloride*, m. p. 211—212°, *stannochloride*, m. p. 115—116°, and *picrate*, pale yellow prisms, m. p. 147—148°.

By distillation with zinc dust in a current of hydrogen, 2 : 3-dimethyl-Δ^2-tetrahydropyridine hydrochloride yields 2 : 3-*dimethylpyridine*, which is isomeric with the lutidines hitherto known; it forms a crystalline, hygroscopic *hydrochloride*, *aurichloride*, m. p. 162—164°, *platinichloride*, m. p. 195°, *mercurichloride*, m. p. 191—193°, and *picrate*, m. p. 183—184°, and yields quinolinic acid by oxidation with alkaline potassium permanganate. C. S.

4-Substituted Piperidines. Ernst Koenigs and Ludwig Neumann (*Ber.*, 1915, **48**, 956—963).—Emmert and Dorn (this vol., i, 584) had reduced 4-hydroxy- and 4-amino-pyridine to the corresponding piperidines, as these compounds enter into the composition of many alkaloids. The present authors had the same interest in this subject and had already obtained results which coincide with those of Emmert and Dorn.

4-Hydroxypyridine was prepared from 4-pyrone (Haitinger and Lieben, A., 1885, 47) and reduced to 4-hydroxypiperidine. In addition

to the data recorded by Emmert and Dorn, the m. p. of the hydrochloride is given as 146—148°, that of the aurichloride as 206—209°, whilst the *platinichloride* was obtained in long, yellowish-red needles, m. p. 184—187° (decomp.), and the *sulphate* in white needles, m. p. 263—266°.

4-Aminopyridine was prepared by way of chelidamic acid, chlorochelidamic acid, and aminochelidamic acid (Kinne, *Diss.*, Breslau, 1914) and also reduced to 4-aminopiperidine.

The authors were especially interested in the reduction of 4-pyridyl ethers. The 4-pyridyl methyl and ethyl ethers were obtained by the method of Haitinger and Lieben (*ibid.*, 811, 965). The propyl and phenyl ethers have also been obtained by the action of sodium propoxide or phenoxide on 4-chloropyridine. *4-Pyridyl propyl ether* (*4-propoxypyridine*), $C_8H_{11}ON$, is an alkaline liquid, b. p. 218—220°/742 mm., which forms a *hydrochloride*, long, white needles, m. p. 156—157°, an *aurichloride*, pale yellow, slender needles, m. p. 147—150°, a *platinichloride*, ochre-yellow prisms, m. p. 192—195°, and a *picrate*, m. p. 120—124°. *4-Pyridyl phenyl ether* (*4-phenoxypyridine*), $C_{11}H_9ON$, has m. p. 45—46°, b. p. 134—136°/10 mm., 277—279°/760 mm., and forms a *hydrochloride*, m. p. 177—178°, a *platinichloride* m. p. 196—197°, an *aurichloride*, m. p. 159—162°, and a *chromate*, m. p. 130° (decomp.). When these ethers were reduced by sodium and alcohol, none of the expected piperidyl ethers was obtained. The reaction proceeded too far with about 90% of the material, the product being piperidine, whilst the remainder was only partly reduced to tetrahydropyridyl ethers. These were separated from the later fractions of the steam distillates. *4-Tetrahydropyridyl methyl ether* (*4-methoxypiperideine*), $C_6H_{11}ON$, is a clear liquid, having the odour of piperidine, b. p. 61—65°/11 mm. (*aurichloride*), and *4-phenoxypiperideine*, b. p. 143—146°/13 mm., is readily hydrolysed by boiling hydrochloric acid to the *hydrochloride* of *4-hydroxypiperideine*, C_5H_9ON,HCl,H_2O, m. p. 94—96°; (anhydrous), 147—149°.

The above 4-hydroxypiperidine was readily converted into 4-bromo- and 4-iodo-piperidine, but not into the chloro-derivative, by the action of the concentrated hydracid in a sealed tube. 4-Bromopiperidine forms a *hydrobromide*, $C_5H_{10}NBr,HBr$, m. p. 192—193°, *hydrochloride*, m. p. 188—189°, *aurichloride*, m. p. 171—172°, *platinichloride*, m. p. 213—214°, and mercurichloride. 4-Iodopiperidine forms a *hydriodide*, prismatic needles, m. p. 170—172°, *hydrochloride*, m. p. 175—178°, *aurichloride*, m. p. 147° (decomp.), *platinichloride*, m. p. 187° (decomp.), and mercurichloride. The free bases could not be isolated.

J. C. W.

New Indole Reaction. Oskar Baudisch (*Zeitsch. physiol. Chem.*, 1915, **94**, 132—135).—This reaction is specially intended for the easy recognition of cholera vibrions which, according to the author, surpass all other bacteria in their power of rapidly transforming tryptophan into indole. The reaction is applied as follows: A few drops of nitromethane are mixed with the agar culture medium, from which the usual agar plates are then prepared. The material for investigation, or a preliminary culture prepared from it, is now placed on the plates

and incubated for eight to sixteen hours. The suspected colonies with the surrounding agar are transferred to a test-tube and boiled with dilute potassium hydroxide solution. After cooling, 1 c.c. of amyl alcohol and then an excess of sulphuric acid are added with continual shaking. On again warming, the amyl alcohol separates and is coloured red or pink if cholera vibrions were present in the suspected material.

H. W. B.

Some Reactions of Indole. W. MADELUNG and M. TENCER (*Ber.*, 1915, **48**, 953—955).—When indole is heated with sulphur at 180—190°, it forms a *compound*, $C_{14}H_{12}N_2$, m. p. 326° (decomp.). This is sensitive towards oxidising agents; the strongly fluorescent solutions gradually become green even in the air, whilst concentrated nitric acid produces isatin. It is not basic and may be a 1-anilinoindole. 2-Methylindole does not react in this way.

A very ready scission of indole was found to take place when an attempt was made to prepare the anil of indolone,

$$NPh{:}C\begin{<}CH{:}N\\ C_6H_4\end{<}$$

by the action of nitrosobenzene and a few drops of alcoholic potassium hydroxide on indole. The chief product was phenylcarbylamine, with azobenzene as a secondary product. J. C. W.

Sulphur Derivatives of Indole and Methylindole. W. MADELUNG and M. TENCER (*Ber.*, 1915, **48**, 949—953).—In the hope of obtaining 3-thiolindole, magnesium indolyl bromide has been treated with sulphur and sulphur chloride, but the product of the reaction was found to be a very stable, non-basic substance which must be regarded as composed of two indole residues linked by the nitrogen atoms through a sulphur atom. Sulphur dioxide reacted with the organomagnesium compound to form the corresponding sulphoxide.

Finely powdered sulphur was added to a solution of magnesium indolyl bromide, made by adding indole to magnesium ethyl bromide, when *di-indolyl sulphide*, $C_{16}H_{12}N_2S$, separated. This forms colourless needles from xylene, m. p. 232°, and the corresponding *di-2-methylindolyl sulphide* has m. p. 226°. The solution of the Grignard compound was also treated with ethereal sulphur dioxide, when *di-indolyl sulphoxide*, $C_{16}H_{12}ON_2S$, was obtained, in colourless needles, m. p. 157° (decomp.), which yielded the above sulphide on reduction with zinc dust and glacial acetic acid. J. C. W.

Preparation of 2-Cyanoquinoline and 1-Cyano*iso*quinoline. L. GIVAUDAN, VERNIER, and A. KAUFMANN (D.R.-P. 280973; from *J. Soc. Chem. Ind.*, 1915, **34**, 416).—2-*Cyanoquinoline*, m. p. 94°, and 1-*cyano*isoquinoline, m. p. 78°, are prepared by treating 2-cyano-1-benzoyl-1 : 2-dihydroquinoline and 1-cyano-2-benzoyl-1 : 2-dihydro*iso*quinoline, respectively, with phosphorus pentachloride, sulphuryl chloride, or thionyl chloride in an anhydrous, inert diluent. They may be applied to the production of dyes or pharmaceutical materials.

J. C. W.

Preparation of the [Salicylic and *o*-Acetoxybenzoic] Esters of 8-Hydroxyquinoline. R. WOLFFENSTEIN (D.R.-P. 281007; from *J. Soc. Chem. Ind.*, 1915, **34**, 452).—The base is treated with the acid chlorides. The esters have an important influence on the metabolism of purine derivatives. J. C. W.

Preparation of Homologues and Substitution Products of 2-Piperonylquinoline-4-carboxylic Acid. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 281603; from *J. Soc. Chem. Ind.*, 1915, **34**, 637).—Homologues or substitution products of aniline are condensed with piperonaldehyde and pyruvic acid. The products, for example, 6-*methyl*-, 6-*hydroxy*-, and 8-*methoxy*-2-*piperonylquinoline*-4-*carboxylic acids*, are tasteless. J. C. W.

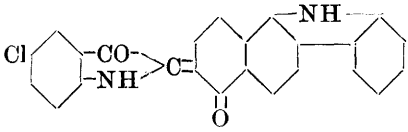
Preparation of Esters of 2-Piperonylquinoline-4-carboxylic Acid and its Derivatives. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 281136; from *J. Soc. Chem. Ind.*, 1915, **34**, 637).—The acids are treated with alcohols or phenols in the usual way. The esters are tasteless, and exhibit the therapeutic properties of 2-phenylquinoline-4-carboxylic acid, without promoting the separation of uric acid. J. C. W.

Preparation of Derivatives (Arylides) of 2-Piperonylquinoline-4-carboxylic Acid and its Homologues. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 281097, addition to D.R.-P. 252643, A., 1913, i, 92).—Arylides, like the amides (this vol., i, 161), are prepared from the acid chlorides, which are obtained by the action of thionyl chloride. 2-*Piperonylquinoline*-4-*carboxyanilide* forms yellow needles, m. p. 241°; 2-*piperonyl*-6-*methylquinoline*-4-*carboxy*-p-*toluidide* is a yellow, crystalline powder, decomp. 255—260°; 2-*piperonylquinoline*-4-*carboxy*-p-*phenetidide* crystallises in greyish-brown leaflets, m. p. 224°, and the p-*ethylcarbonatoanilide*, from ethyl *p*-aminobenzoate, forms yellow granules, m. p. 248°. J. C. W.

Preparation of Quinolyl Ketones. VEREINIGTE CHININFABRIKEN, ZIMMER & Co. (D.R.-P. 280970; addition to D.R.-P. 268830, A., 1914, i, 575; from *J. Soc. Chem. Ind.*, 1915, **34**, 575).—Esters of quinolinylacetic acid, or nuclear-substituted products, are alkylated, and the resulting esters are converted into alkyl homologues of quinolyl methyl ketones or their nuclear-substituted products. J. C. W.

Preparation of Monosulphonic Acids of Carbazole and its *N*-Alkyl Derivatives. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 275795).—The hitherto unknown monosulphonic acids can be obtained by sulphonation in the presence of an inert diluent, such as nitrobenzene, halogenated benzenes, or glacial acetic acid. For example, carbazole or *N*-methylcarbazole is treated with concentrated or 20% fuming sulphuric acid in about ten times as much nitrobenzene at 20° or 70—80°. The *sodium* salt of *N*-methylcarbazolemonosulphonic acid crystallises in colourless needles from water, and *sodium carbazolesulphonate* in leaflets. The acids may be used in the preparation of dyes. J. C. W.

Preparation of a Black Vat Dye. KALLE & Co. (Swiss Pat. 65545. Compare D.R.-P. 241997). — A *dye* of the annexed constitution is obtained by heating *p*-chloroisatin-*α*-*p*-chloroanilide and 5-oxy-2:1-naphthacarbazole with acetic anhydride. It gives a clear yellow hyposulphite vat and dyes textiles pure black.



J. C. W.

Condensation of β-Diketones with Diamines. N. A. ROSANOV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 611—613).—The numerous investigations by Knorr and his collaborators (compare A., 1894, i, 545, 546; 1897, i, 108, 110, 111; 1903, i, 659) on pyrazole derivatives have shown that by the action of hydrazine on different β-diketones it is possible to obtain a five-membered ring with two neighbouring nitrogen atoms. Thus, acetylacetone and hydrazine yield 3:5-dimethylpyrazole (compare Rosengarten, A., 1894, i, 546), the structure of which assumes that the acetylacetone reacts in its enolic form. Similar ring-closure is effected by the action of hydrazine on oxalic and succinic acids (compare Sernagiotto and Paravagno, A., 1914, i, 812) and by that of *o*-phenylenediamine on acetyl- and benzoyl-acetones (compare Thiele and Steimmig, A., 1907, i, 352), seven-membered rings being obtained in the latter case.

The author finds that seven-membered rings are also formed by the action of ethylenediamine on acetylacetone and on γ-methylpentane-βδ-dione, the reaction in the former instance being represented by the equation:

$$OH\cdot CMe{:}CHAc + NH_2\cdot CH_2\cdot CH_2\cdot NH_2 = 2H_2O + CH\begin{cases}CMe\cdot NH\cdot CH_2\\ CMe{:}N\text{—}CH_2\end{cases}.$$

The *compound*, $C_7H_{12}N_2$, thus obtained, forms large needles, m. p. 112—113°. The *compound*, $CMe\begin{cases}CMe\cdot NH\cdot CH_2\\ CMe{:}N\text{—}CH_2\end{cases}$, yielded by ethylenediamine and γ-methylpentane-βδ-dione, forms large needles, m. p. 154—155°. The structures given for these compounds require confirmation.

T. H. P.

Constitution of the So-called Dithiourimidoacetylacetone. WILLIAM J. HALE (*J. Amer. Chem. Soc.*, 1915, **37**, 1544—1552).—When concentrated sulphuric acid is added to an alcoholic solution of acetylacetone and thiocarbamide, acetylacetonethiocarbamide is produced (compare Hale and Williams, this vol., i, 168). If, however, only a very small quantity of acid is used, the product known as dithiourimidoacetylacetone (Evans, A., 1894, i, 111) is obtained.

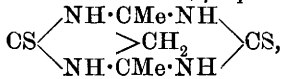
It is now shown that the latter compound is 6-thiocarbamido-2-thio-4:6-dimethyl-1:2:5:6-tetrahydropyrimidine,

$$NH_2\cdot CS\cdot NH\cdot CMe\begin{cases}NH\text{—}CS\\ CH_2\cdot CMe\end{cases}N,$$

and that it can be obtained in a yield of 91% of the theoretical by heating a concentrated aqueous solution of thiocarbamide (2 mols.) with acetylacetone (1 mol.) at the temperature of the steam-bath; it has

m. p. 192°, crystallises in monoclinic prisms, and its aqueous solution readily blackens mercuric oxide. By prolonged boiling with an aqueous solution of chloroacetic acid it yields 6-carbamido-4 : 6-dimethyl-1 : 2 : 5 : 6-tetrahydro-2-pyrimidone (Haan, A., 1908, i, 578).

When an alcoholic solution of thiocarbamide and acetylacetone is exposed to sunlight for several months, *βδ-pentanedithiocarbamide*,

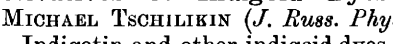


is sometimes obtained, which forms colourless crystals, decomposes at about 265°, and does not blacken mercuric oxide; it is desulphurised by boiling it for five hours with chloroacetic acid with formation of βδ-pentanedicarbamide (Haan, *loc. cit.*). E. G.

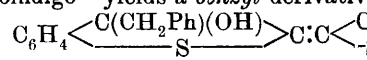
Preparation of Glucosides of the Purine Series and their Derivatives. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 281008; from *J. Soc. Chem. Ind.*, 1915, **34**, 636).—Based on E. Fischer's work (A., 1914, i, 333). J. C. W.

Preparation of Oxidation Products of the Indigo Series. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 281050; addition to D.R.-P. 276808; from *J. Soc. Chem. Ind.*, 1915, **34**, 545).—The oxidation product of isatin described in the chief patent (this vol., i, 65) may be obtained under the same conditions from indigotin. Analogous compounds may be prepared from derivatives of indigotin. J. C. W.

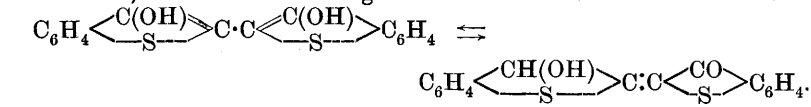
Leuco-derivatives of Indigoid Dyes and their Etherification. MICHAEL TSCHILIKIN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 539—552).—Indigotin and other indigoid dyes are characterised by the presence of an indophoric grouping, which determines their principal chemical properties (A., 1912, i, 654). One of the fundamental reactions consists in the formation, on reduction, of two isomeric leuco-derivatives (A., 1914, i, 191); etherification of these gives only derivatives of the keto-form, that is, quinols and not true ethers. A number of these derivatives have been prepared, the reaction being carried out on the water-bath in an atmosphere of hydrogen, sodium hyposulphite being used as reducing agent.

Methylquinolindigotin,  prepared by the action of methyl sulphate on leuco-indigotin, forms crystals which appear almost black by reflected light, but are nearly transparent, m. p. about 209°; it begins to decompose at 235°, and yields an olive-green coloration with concentrated sulphuric acid. The corresponding *ethyl* derivative, $C_{18}H_{16}O_2N_2$, m. p. about 216° (decomp.), forms a bright yellow zinc salt, and the *amyl* derivative, $C_{21}H_{23}O_2N_2$, m. p. 160—162°, gives a red solution in methyl alcohol, and a greenish-blue solution in sulphuric acid.

"Leucothioindigo" yields a *benzyl* derivative,

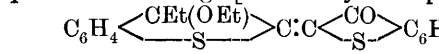


which forms a red, microcrystalline powder, m. p. about 56—57°, and has the normal molecular weight in freezing benzene. It is evident, therefore, that "leucothioindigo" also exhibits keto-enolic isomerism:

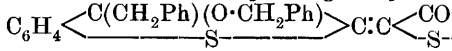


The quinols of indigotin, with the exception of the methyl derivative, are difficult to obtain in the crystalline form, owing to the readiness with which they resinify, but those of "thioindigo" crystallise readily and often yield well-developed, colourless crystals.

The *ethylquinol* of thioindigo [2:2′-bisoxythionaphthen]

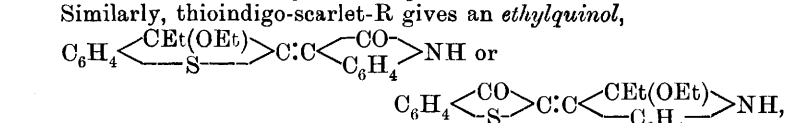


prepared by the action of ethyl iodide on the leuco-derivative, forms white crystals, m. p. 104—105°, exhibits normal cryoscopic and ebullioscopic behaviour in benzene, and gives a bright orange coloration with sulphuric acid. The corresponding *benzyl* derivative,

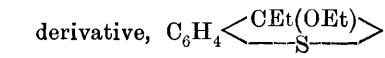


forms small, rose-red crystals, m. p. 211—211·5°.

Similarly, thioindigo-scarlet-R gives an *ethylquinol*,



which forms white crystals, m. p. 166·5°, gives an orange coloration with concentrated sulphuric acid and exhibits the normal molecular weight in freezing benzene. The corresponding *benzyl* derivative forms a yellowish-white, microcrystalline powder, m. p. 198·5—200°, and gives an orange coloration with concentrated sulphuric acid.

Thioindigo scarlet-GG, or Ciba scarlet-G, gives an analogous *ethyl* derivative,  , which forms a bright orange-yellow, microcrystalline powder, m. p. 194—195°, and gives a grass-green coloration with concentrated sulphuric acid.

T. H. P.

Salts of Certain Aminoazo-compounds. L. Casale and Maria Casale-Sacchi (*Gazzetta*, 1915, **45**, i, 490—501. Compare A., 1914, i, 1180).—The authors have investigated the sulphates, hydrochlorides, and nitrates formed by all the aminoazo-compounds derived from α-naphthylamine. All these compounds form stable sulphates containing 1 mol. of base and 1 mol. of acid; only in certain instances is a normal salt, containing 2 mols. of base and 1 mol. of acid, formed. Two series of hydrochlorides are formed, those with 1 mol. of acid being stable, and those with 2 mols. of acid undergoing rapid change into the first in the air; with 1-naphthaleneazo-1-naphthylamine, however, both hydrochlorides are stable. In all cases, stable salts are formed with 1 mol. of nitric acid, and unstable ones with 2 mols.; the latter salts, when fused, undergo a characteristic decomposition, which

is to be described in a subsequent communication. Both the nitrates of 1-naphthaleneazo-1-naphthylamine are, however, stable. All of these salts crystallise well, usually in green prisms with reflexion varying from red to violet; they dissolve in the ordinary hydroxylic, organic solvents, and are hydrolysed by water.

Estimation of nitrogen in the unstable nitrates by the combustion method yields untrustworthy results, but the nitric acid present may be estimated volumetrically in presence of methyl-red, the salt being titrated in suspension in water.

4-*Benzeneazo*-1-*naphthylamine sulphate*, $C_{16}H_{13}N_3,H_2SO_4$, forms long, green prisms with red or blue reflexion, m. p. 214—215°. The *dihydrochloride* forms a violet-green, crystalline precipitate; the *monohydrochloride*, grass-green prisms, m. p. 205°, and the *dinitrate*, blood-red crystals, which change rapidly into the green mononitrate.

4-o-*Tolueneazo*-1-*naphthylamine sulphate*, $C_{17}H_{15}N_3,H_2SO_4$, forms long, green, prismatic needles with metallic lustre, m. p. 195—196° (decomp.); the normal *sulphate*, $2C_{17}H_{15}N_3,H_2SO_4$, golden-yellow leaflets, m. p. 163° (decomp.); the dark green *aihydrochloride* yields the *monohydrochloride* when crystallised from acetic acid; the *dinitrate* forms a crystalline mass of a deep coffee colour and when the fused salt is heated on a water-bath, it explodes and inflames at about 80°; the *mononitrate*, obtained by crystallising the dinitrate from hot alcohol, forms emerald-green prisms, m. p. 170°.

4-m-*Tolueneazo*-1-*naphthylamine sulphate*, $C_{17}H_{15}N_3,H_2SO_4$, forms long, rectangular, bronze-green laminæ, m. p. 189°; the *monohydrochloride*, pale green prisms with blue reflexion, and the *mononitrate*, violet-green crystals, m. p. 172°.

4-p-*Tolueneazo*-1-*naphthylamine sulphate*, $C_{17}H_{15}N_3,H_2SO_4$, forms green, prismatic needles with red reflexion, m. p. 211°; the *dihydrochloride*, a violet, crystalline precipitate with dark green reflexion; the *monohydrochloride*, short, grass-green prisms, m. p. 211° (decomp.); the *dinitrate*, a dark greenish-coffee coloured, crystalline precipitate, and the *mononitrate*, violet, prismatic needles with green reflexion, m. p. 163°.

4-o-*Methoxybenzeneazo*-1-*naphthylamine sulphate*, $C_{17}H_{15}ON_3,H_2SO_4$, forms short, olive-green needles, m. p. 173°; the *dihydrochloride*, coffee-coloured crystals with green reflexion; the *monohydrochloride*, dark green crystals with metallic lustre, m. p. 194—195°; the *dinitrate*, a deep green, crystalline powder, and the *mononitrate*, large aggregates of emerald-green prisms, m. p. 173°.

4-o-*Ethoxybenzeneazo*-1-*naphthylamine sulphate*, $C_{18}H_{17}ON_3,H_2SO_4$, forms grass-green prisms, m. p. 182° (decomp.); the *dihydrochloride* is similar to those described above; the *monohydrochloride* forms pale green, prismatic needles, m. p. 195°; the *dinitrate* and the *mononitrate*, m. p. 158—159°, were prepared.

4-*Naphthaleneazo*-1-*naphthylamine sulphate*, $C_{20}H_{15}N_3,H_2SO_4$, forms dark green prisms, m. p. 163°; the *dihydrochloride*, green prisms, turning red suddenly at 140° and brown at about 190°, m. p. 201—202°; the *monohydrochloride*, short, blackish-green, opaque needles, turning brown at above 230°, and the *dinitrate*, dark green prisms with bronze reflexion, exploding at 139—140°.

4-o-*Nitrobenzeneazo*-1-*naphthylamine sulphate*, $C_{16}H_{12}O_2N_4,H_2SO_4$, forms coffee-coloured prisms with green reflexion, m. p. 217—218°; the *normal sulphate*, $2C_{16}H_{12}O_2N_4,H_2SO_4$, dark brick-red needles, m. p. 200°; the *monohydrochloride*, green prisms, m. p. 187°, and the *mononitrate*, emerald-green prisms, m. p. 165—166°. T. H. P.

Experiments on the Synthesis of Polypeptides, Peptones, and Proteins by means of Ferments. EMIL ABDERHALDEN (*Chem. Zentr.*, 1915, i, 899; from *Fermentforschung*, **1**, 47—54).—From the work of Bayliss (A., 1913, i, 919) it seemed probable that the degradation and the synthesis of a substance could be effected by one and the same enzyme. Numerous experiments with pepsin, trypsin, and erepsin on the synthesis of proteins from their degradation products were unsuccessful, but the treatment of mixtures of amino-acids from definite organs with the juice from the same organ led to the desired result, as after some months there was a decrease in amino-nitrogen which could be explained in no other way, and also the coagulation test showed the presence of protein. The enzymes of the cell exert, therefore, a specific action according to the nature of the cell. Syntheses of proteins from peptones were also effected in a similar way. G. F. M.

Diazo-reaction of Protein. HERMANN PAULY (*Zeitsch. physiol. Chem.*, 1915, **94**, 284—290).—The diazo-reaction of protein is dependent on the presence of tyrosine or of histidine in the protein molecule. Since the dyes resulting from the direct interaction of tyrosine and histidine with diazobenzenesulphonic acid were found to be too soluble to be readily isolated and purified, the corresponding dyes from the sodium salt of *p*-aminophenylarsinic acid (atoxyl) have been prepared and their properties investigated. *Tyrosinebisazobenzenearsinic acid*, $C_9H_9O_3N(N{:}N{\cdot}C_6H_4{\cdot}AsO_3H_2)_2,2H_2O$, is prepared by adding a diazotised solution of atoxyl in the calculated quantity of *N*-hydrochloric acid to an alkaline solution of tyrosine. On acidifying, the dye is precipitated as a yellow, microcrystalline powder which is insoluble in the usual organic solvents. *Histidinebisazobenzenearsinic acid*, $C_6H_7O_2N_3(N{:}N{\cdot}C_6H_4{\cdot}AsO_3H_2)_2$, prepared in a similar way, has similar properties. Both compounds may be boiled with strong mineral acids without evolution of nitrogen occurring, which indicates that the diazo-groups are attached to carbon atoms rather than to the amino- or imino-nitrogen atoms of the amino-acids. H. W. B.

Combination of Protein with Halogen Acids. J. H. LONG and MARY HULL (*J. Amer. Chem. Soc.*, 1915, **37**, 1593—1606).—Determinations of the proportions in which proteins and halogen acids combine have hitherto been usually made by ascertaining the amount of acid held by a given weight of the protein when an excess is added and afterwards titrated in presence of a suitable indicator. It is now shown that when the amounts of halogen acids which combine with casein, fibrin, and egg-albumin are estimated in this way, the results obtained are low and not exactly proportional to the molecular weights of the acids. The discrepancies seem to be chiefly due to the partial

dissociation of the protein salt. If these proteins are treated with excess of 0·2*N*-halogen acid and the mixtures are evaporated by leaving them in a desiccator, first over sulphuric acid and afterwards over alkali hydroxide, and are finally dried at 75°, salts containing constant weights of acid are produced. The amounts of acid in these salts are not proportional to the molecular weights of the acids, but the combining proportion is relatively greater for hydriodic than for hydrobromic acid, and greater for the latter than for hydrochloric acid. All the compounds contain many times as much acid as is suggested by the titration method, and they readily dissociate when treated with water.

If the mixtures of acid and protein are evaporated on the water-bath instead of being dried at a low temperature, the proportions of hydrochloric and hydrobromic acids in the dry residues are approximately the same as in the latter case. In the case of hydriodic acid, however, there is no definite limit to the quantity of iodine held by the protein, and it is probable that not only does the acid combine with the protein, but that iodine is substituted in the nucleus of the protein molecule. As much as 75% of the weight of the protein may be so held, and the product has a brown colour and no longer gives protein reactions. E. G.

Origin of the Humin Formed by the Acid Hydrolysis of Proteins. Ross Aiken Gortner and Morris J. Blish (*J. Amer. Chem. Soc.*, 1915, **37**, 1630—1636).—Experiments are described on the acid hydrolysis of zein, gliadin, mixtures of zein and tryptophan, zein and histidine, zein and dextrose, and gliadin and dextrose with particular reference to the formation of humin. The results indicate that the humin nitrogen has its origin in the tryptophan nucleus. Humin is not formed when pure tryptophan is boiled with mineral acid, but in presence of protein or carbohydrate a considerable quantity of humin is produced. The formation of the humin is probably due to the condensation of an aldehyde with the NH-group of the tryptophan nucleus. When a large quantity of carbohydrate is present, nearly 90% of the tryptophan nitrogen remains in the humin fraction, and it is suggested that this fact might be utilised for the approximate estimation of tryptophan in proteins. Histidine has no influence on the formation of humin. The adsorption of ammonia by non-nitrogenous humins formed from carbohydrates is not an important factor in the production of humin nitrogen. E. G.

Action of Chymosin [Rennet] and Pepsin. II. New Method for Abolishing the Parallelism between the Action of Chymosin and Pepsin. Olof Hammarsten (*Zeitsch. physiol. Chem.*, 1915, **94**, 104—127. Compare A., 1914, i, 1100).—The mucous membrane of the calf's stomach is ground with salt in a mortar and then spread out in thin layers to dry. The product can be preserved for months without losing its activity.

To prepare solutions of the active enzymes, the salt powder is extracted with a small quantity of water. The extract (A), consisting of the enzymes in saturated salt solution, is separated from the residue

(B), which still contains enzyme and undissolved salt. From both (A) and (B), by dialysis or by treatment with 0·2% hydrochloric acid, solutions are obtained which contain the enzymes chymosin and pepsin in widely differing proportions. Whereas solution A is usually very strongly proteolytic, solution B contains scarcely any pepsin. On the other hand, the chymosin in solution B may be five to seven times as active as that in solution A. The proteolytic and clotting powers of extracts of the calf's stomach must therefore be due to the presence of two separate enzymes. H. W. B.

Identity of Oxidation Enzymes. (Mlle.) G. Woker (*Arch. Sci. phys. nat.*, 1915, [iv], **39**, 405—414. Compare A., 1914, i, 603).—The author has developed the theory that the several enzyme actions, for example, peroxydase, reductase, catalase, are due to the same agent, which has an aldehydic character. Bach (this vol., i, 184) has quoted experiments which appear to contradict this hypothesis: the author maintains her former views. E. F. A.

Reductase of Liver and Kidney. III. The Influence of Heat, Light, and Radium Radiations on the Activity of Reductase. David Fraser Harris and Henry Jermain Maude Creighton (*J. Biol. Chem.*, 1915, **21**, 303—308).—Heat inhibits the activity of reductase; this increases with temperature, and permanent inhibition occurs at 70—75°. Light and radium radiations have no effect. W. D. H.

Chemical Nature of Catalase. P. Waentig and W. Gierisch (*Chem. Zentr.*, 1915, i, 955—956; from *Fermentforschung*, **1**, 165—195).—The inactivation of catalase by proteolytic enzymes cannot be regarded as certain proof of its protein character, and the examination of the purest obtainable preparations was undertaken. An aqueous extract of bullock's liver was precipitated with alcohol, and the catalase, which can only be completely extracted from the precipitate with great difficulty on account of the adsorptive action of accompanying impurities and alterations in the enzyme itself, was further purified by: (1) Fractional extraction, the middle extracts being the purest; (2) self-purification by long keeping of the extract at low temperatures with preservatives, whereby a considerable portion of the non-ferments was precipitated; (3) repetition of the precipitation with alcohol, whereby a large portion of the aqueous extractive remained in solution; (4) dialysis, although often accompanied by loss of activity; (5) adsorption in finely divided substances.

After purification, catalase proved to be a coagulable protein, precipitated in the cold by mineral acids, but not by acetic acid. Coagulation by heat is preceded by inactivation. The precipitates with alcohol and ammonium sulphate are active reversible gels which only slowly undergo change. The limit concentrations depend on the accompanying impurities. Alkaloidal reagents and bromine water also precipitate catalase. The protein reactions all give a positive result, the biuret test giving a bluish-violet colour.

The nitrogen content of the catalase increases with increasing purity

to at least 14%. Mineral matter is almost absent, although iron and phosphorus are always present, but it is doubtful whether they are integral constituents, as it is certain that catalase is not a nucleoprotein. A positive result with Molisch's test indicated a sugar group, but in an addendum the author states that a further purified specimen containing 15·45% of nitrogen gave this test but faintly. The ash of this preparation still contained iron and phosphorus. G. F. M.

Effect of Poisons on an Enzymatic Process. III. Compounds of Arsenic and Phosphorus. C. G. SANTESSON (*Chem. Zentr.*, 1915, i, 556; from *Skand. Arch. Physiol.*, 1914, **32**, 405—428).—The influence of the following compounds of arsenic on the action of muscle catalase has been investigated: arsenious oxide, orthoarsenic acid, sodium metarsenite, normal sodium orthoarsenate, sodium cacodylate, atoxyl, and neosalvarsan. Relatively concentrated solutions of arsenious oxide, orthoarsenic acid, sodium metarsenite, and neosalvarsan (which is thereby decomposed) have an inhibiting effect, increasing in the given order; the other substances have an unimportant, generally slightly depressing influence. In more dilute solution, at an optimum concentration which varied considerably with the individual compounds, the greater number of the substances have a tendency to increase the catalase action, but this effect is not observed with sodium metarsenite or sodium arsenate. In the undecomposed state, the organic compounds have a very slight effect. Phosphorus water likewise depresses and delays catalysis. H. W.

Aminophenyl Arsenic Compounds. PARKE, DAVIS & Co. (U.S. Pat. 1119279; from *J. Soc. Chem. Ind.*, 1915, **34**, 451).—Aminophenyl arsenic derivatives are treated with carbethoxy compounds, such as ethyl chlorocarbonate, and then, if desired, nitrated and finally reduced. The products, of which *p*-urethanophenylarsenoxide, $CO_2Et{\cdot}NH{\cdot}C_6H_4{\cdot}AsO$, and carbethoxy-4 : 5-diaminophenylarsenoxide are examples, are said to be useful in cases of swine cholera. J. C. W.

Preparation of Heavy-metal Compounds of Aromatic Arsenic Compounds. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 275216; addition to D.R.-P. 268220, etc.; A., 1914, i, 345, 761, 1010).—Instead of using arseno-compounds, derivatives of the ultimate products of the reduction of arsinic acids (A., 1913, i, 117), namely, aromatic arsines, provided that the nucleus contains a salt-forming group (hydroxyl or amino), may also be used for the preparation of heavy-metal compounds of the type described in the earlier patents. The metal seems to be attached by the exercise of the residual affinity of the arsenic atom.

3-Amino-4-hydroxyphenylarsine gives a brown compound with gold chloride, a black with silver nitrate, and a yellowish-red with cupric chloride. 4-*Hydroxy*-3-*urethanophenylarsine*,

$$CO_2Et{\cdot}NH{\cdot}C_6H_3(OH){\cdot}AsH_2,$$

a white powder, obtained by the reduction of the corresponding arsinic acid (*ibid.*), gives a black compound with palladous chloride, and p-*acetylaminophenylarsine*, $NHAc{\cdot}C_6H_4{\cdot}AsH_2$, a white powder,

insoluble in acids or alkalis, forms a yellowish-red compound with cupric chloride. J. C. W.

Arsenobenzoic Acids. A. MICHAELIS (*Ber.*, 1915, **48**, 870—873). —*o*- and *p*-Arsenobenzoic acids, $As_2(C_6H_4{\cdot}CO_2H)_2$, have been prepared from the corresponding carboxyphenylarsinic acids,

$$CO_2H{\cdot}C_6H_4{\cdot}AsO(OH)_2,$$

which in their turn are derived from the tolylarsinic acids.

p-Carboxyphenylarsinic acid (*p*-benzarsinic acid) was obtained by heating *p*-tolylarsinic acid with nitric acid (D 1·2) for twelve hours at 150°. It forms leaflets, whilst the tolylarsinic acid crystallises in needles. Otherwise, the acids are only distinguishable by means of their *aniline* salts, which form long needles; the salt of *p*-carboxyphenylarsinic acid has no m. p., whilst that of *p*-tolylarsinic acid has m. p. 119°. The benzarsinic acid was transformed into *p*-carboxyphenylarsenious acid, $CO_2H{\cdot}C_6H_4{\cdot}As(OH)_2$, by La Coste's method (A., 1881, 168, 903). This was dissolved in just sufficient boiling water and mixed with an excess of solid phosphorous acid, when p-*arsenobenzoic acid* separated as an insoluble, pale yellow powder, which forms soluble, neutral, alkali salts.

The acids in the ortho-series are more soluble than their isomerides. o-*Carboxyphenylarsinic acid* (o-*benzarsinic acid*) also differs in forming a very soluble aniline salt. It was treated with red phosphorus and hydriodic acid, and the solution of the arseniodide, $CO_2H{\cdot}C_6H_4{\cdot}AsI_2$, was rendered just alkaline and boiled with phosphorous acid, when o-*arsenobenzoic acid* separated as a heavy, yellow powder.

Both arsenobenzoic acids are very toxic, and cause pronounced glycosuria and albuminuria. J. C. W.

Preparation of Azo-dyes containing the Arseno-group. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 271271). —Azo-dyes containing the arsinic acid or arsenoxide group can be reduced by hypophosphorous acid without affecting the azo-group. The arsenoazo-dyes so obtained have therapeutic value. Examples: (1) The dye obtained by coupling diazotised 3-amino-4-hydroxyphenylarsinic acid with phloroglucinol is boiled with 35% hypophosphorous acid, giving a red dye. (2) The dye obtained from *m*-aminophenylarsinic acid and 2-naphthylamine-3 : 6-disulphonic acid gives the reddish-brown dye, $[(SO_3H)_2C_{10}H_4(NH_2){\cdot}N{:}N{\cdot}C_6H_4]_2As_2$. (3) The dye obtained from diazoatoxyl and 1-amino-8-naphthol-3 : 6-disulphonic acid gives a dark powder with metallic lustre. J. C. W.

Mixed Mercury Dialkyls. SIEGFRIED HILPERT and GERHARD GRÜTTNER (*Ber.*, 1915, **48**, 906—915).—From some preliminary experiments, and from the old observations of Frankland, the conclusion is drawn that mixed mercury dialkyls are very sensitive to heat, being decomposed into the two simple mercury dialkyls. The authors have shown that when magnesium phenyl bromide is treated with mercuric chloride, the first product is mercury phenyl bromide, $C_6H_5{\cdot}HgBr$, which then reacts with increased difficulty with more magnesium phenyl bromide to form mercury diphenyl. It seemed

probable, therefore, that mixed mercury dialkyls would be formed if in the second stage a different magnesium compound were employed.

It was soon found that the affinity of the various alkyl radicles for mercury varies considerably, so that it is even possible to displace one alkyl group by another. For example, if mercury phenyl bromide is treated with an excess of magnesium benzyl bromide the sole product is mercury dibenzyl. This indicated that the course to be adopted in the preparation of mixed mercury dialkyls was to apply in the second stage a radicle with less affinity for mercury than the first, and, by avoiding any rise of temperature, such mixed compounds have been prepared in this way.

The affinity of the radicles for mercury rises from phenyl to ethyl and then benzyl. The *o*- and *p*-tolyl radicles could not be attached to the same mercury atom; the mercury *o*-tolyl *p*-tolyl immediately changes into the two mercury ditolyls.

The mixed mercury dialkyls are extremely poisonous, have not been crystallised, and decompose after a short time into the simple dialkyls. That they were individuals and not mixtures was proved by taking advantage of the thermal constants of the speed of crystallisation and crystallising power. For example, an intimate mixture of equimolecular proportions of mercury diphenyl and mercury dibenzyl is liquid at 95°, and, on cooling, the first nuclei appear at 70°, and the speed of crystallisation is then so fast that the mass becomes solid, at that point, in a few seconds. If, now, the substance regarded as mercury phenyl benzyl is inoculated with mercury dibenzyl or mercury diphenyl, not only does no growth of the crystal take place, but it actually dissolves.

Dry, powdered mercury benzyl chloride was added to magnesium phenyl bromide in ether, and, after half-an-hour, the solution was decomposed by 1% sulphuric acid and the ethereal layer was dried and evaporated. The oil was frozen out two or three times from solution in hot alcohol. *Mercury phenyl benzyl*, $Ph{\cdot}Hg{\cdot}CH_2Ph$, decomposes at 80° into mercury, dibenzyl and mercury diphenyl, and changes into a crystalline mass of mercury diphenyl and mercury dibenzyl at the ordinary temperature. Magnesium ethyl bromide and mercury benzyl chloride gave *mercury benzyl ethyl*, $C_9H_{12}Hg$; magnesium phenyl bromide and mercury ethyl chloride gave *mercury phenyl ethyl*, $C_8H_{10}Hg$; magnesium *o*-tolyl bromide and mercury benzyl bromide gave *mercury o-tolyl benzyl*, $CH_2Ph{\cdot}Hg{\cdot}C_6H_4Me$.

The mercury alkyl haloids were prepared by the addition of mercuric haloids to the magnesium compounds (A., 1913, i, 783). Mercury benzyl chloride (Wolff, *ibid.*, 304); *mercury o-tolyl bromide*, $C_7H_7{\cdot}HgBr$, ciliated needles, m. p. 168°, the corresponding *iodide*, hard crystals, m. p. 176—177·5°, and *sulphide*, $C_{14}H_{14}SHg_2$; mercury *p*-tolyl bromide (Pope and Gibson, T., 1912, **101**, 735) and the corresponding *iodide*, m. p. 217°, are described. J. C. W.

Mercury Derivatives of Aromatic Amines. I. The Structure of Primary and Secondary *p*-Aminophenylmercuri-compounds. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Biol. Chem.*, 1915, **20**, 513—520).—Evidence in support

of Dimroth's (A., 1902, i, 656; compare Pesci, A., 1898, i, 648) unimolecular formula, $NR_2 \cdot C_6H_4 \cdot HgX$, for mercuriated arylamines is furnished by the behaviour of *p*-acetoxymercurianiline and *p*-acetoxymercurimethylaniline towards nitrous acid; the former behaves as a primary aromatic amine, yielding diazonium salts which couple with amines and phenols to form azo-compounds, whilst the latter yields a nitrous compound, and thus behaves as a secondary amine. *p*-Acetoxymercurianiline also undergoes condensation with salicylaldehyde, yielding an azomethine.

4-*Acetoxymercuri*-4'-*dimethylaminoazobenzene*, $C_{16}H_{17}O_2N_3Hg$, prepared by diazotising *p*-acetoxymercurianiline and coupling with dimethylaniline in acetic acid solution, forms brick-red crystals with a violet reflex, m. p. 215°, gives with sulphuric acid reddish-brown solutions having a green fluorescence, and forms sparingly soluble salts with nitric and hydrochloric acids.

4-*Acetoxymercuri*-4'-*diethylaminoazobenzene*, obtained from diethylaniline in a similiar manner, crystallises in glistening, orange-brown platelets, which become red at 120°, m. p. 154·5—156° (corr.).

The diazonium salt also couples with phenol and with resorcinol in alkaline solution, yielding p-*acetoxymecuribenzeneazophenol*, orange crystals, m. p. 218—219° (corr.), and p-*acetoxymercuribenzeneazoresorcinol*, a dark brown powder, softening at 160° (decomp. 190—195°).

4-p-*Acetoxymercuribenzeneazo*-1-*naphthylamine*-5-*sulphonic acid*, $C_{18}H_{15}O_5N_3SHg$, from α-naphthylamine-5-sulphonic acid, forms a glistening, brownish-black, microcrystalline powder (decomp. 280°).

Salicylidene-p-*acetoxymercurianiline*, prepared by heating *p*-acetoxymercurianiline with salicylaldehyde in alcoholic solution, forms yellow microcrystals, darkening at 140°, m. p. about 185° (decomp.).

On treatment with sodium nitrite in acetic acid solution, *p*-acetoxymercurimethylaniline yields p-*acetoxymercurinitrosomethylaniline*, pale drab-coloured, hexagonal platelets, m. p. 183—184° (corr., decomp.), which gives an olive coloration with phenol and sulphuric acid.

5-*Acetoxymercuri*-o-*toluidine*, prepared by rapidly adding an alcoholic solution of *o*-toluidine (3 mol.) to mercuric acetate (1 mol.) dissolved in 50% alcohol (compare Schrauth and Schoeller, A., 1912, i, 930), has m. p. 144—145°, with preliminary softening, and, after diazotisation in acetic acid solution, couples with phenol, yielding 5-*acetoxymercuritoluene*-2-*azophenol*, m. p. 204·5—205° (corr.), with preliminary sintering. F. B.

Preparation of Mercuriated Aminoarylsulphonic Acids. Chemische Fabrik von Friedr. Heyden (D.R.-P. 281009).—The therapeutic value of mercuriated organic compounds depends on the rate at which the metal is set free, and this can be tested by ammonium sulphide. Thus, mercurianiline, which gives mercuric sulphide at once, is too toxic for use, whilst sodium mercuridibenzoate, $Hg(C_6H_4 \cdot CO_2Na)_2$, which is only blackened after three weeks, is too inactive as a drug. Even the compounds of intermediate stability should be chosen with a regard for the personal sensitiveness of the patient to mercury. It is found that the amino-group in such compounds moderates the activity

of the mercury, whilst these compounds can again be "tuned" by the introduction of other substituents.

Thus, metanilic acid, aminophenolsulphonic acid, or sodium hydrogen *m*-aminosulphobenzoate is warmed with freshly precipitated mercuric oxide and water until sodium hydroxide no longer gives a precipitate of mercuric oxide. The aqueous solutions of the sodium salts are then precipitated by alcohol. Sodium mercurimetanilate is only blackened by ammonium sulphide after about twenty-four hours, whilst the hydroxyl group in the aminophenolsulphonic acid compound renders it less stable than the non-phenolic acid. J. C. W.

Preparation of Mercury Compounds of Tyrosine and its Derivatives. F. HOFFMANN-LA ROCHE & Co. (D.R.-P. 279957; from *J. Soc. Chem. Ind.*, 1915, **34**, 451—452).—Alkaline solutions of tyrosine or its derivatives are treated with mercuric salts at the ordinary temperature. The products are sparingly soluble in water, and ammonium sulphide gradually precipitates mercuric sulphide from the solutions. They dissolve readily in alkalis, and these solutions set to jellies after a long time. J. C. W.

Metallic Hæmoglobinates, particularly that of Mercury. R. KOBERT and DAVID (*Chem. Zentr.*, 1914, ii, 1447).—Zinc hæmoglobinate, when freshly prepared, is a red substance which is as sensitive to desiccating agents as hæmoglobin itself. It appears to be a complex salt, since it is completely soluble in very dilute ammonium sulphide. Hæmoglobin from the horse combines with 1·011% of zinc which is approximately equivalent to 2 atoms of zinc to each atom of iron. Zinc hæmoglobinate is insoluble in water containing small quantities of neutral salts. The copper salt is chemically similar to the zinc salt.

Mercury hæmoglobinates have been prepared from mercury salts and horse hæmoglobin. The air-dried substances obtained by the use of mercuric sulphate, mercurous nitrate, mercuric acetate, and mercuric chloride contain 1·7%, 7%, about 8%, and 9·5% Hg respectively. The compounds are readily soluble in dilute ammonia or very dilute ammonium sulphide, less readily in ammonium or sodium carbonate. Internally administered, they are relatively well tolerated. H. W.

Physiological Chemistry.

A Quantitative Respirometer. YANDELL HENDERSON (*Proc. Physiol. Soc.*, 1915; *J. Physiol.*, **49**, xxiv—xxv).—The instrument described and figured interferes as little as possible with normal respiration, and does not involve re-breathing; the apparatus is a recording one, and is satisfactory for observations on man.

W. D. H.

The Action of Oil of Chenopodium on the Circulation and Respiration. WILLIAM SALANT and A. E. LIVINGSTON (*Amer. J. Physiol.*, 1915, **38**, 67—92).—The depressant effects on the circulatory and respiratory mechanisms are described with full details in dogs, cats, and rabbits. W. D. H.

The Colour of the Blood and its Oxygen Content. AUGUST KROGH (*Proc. Physiol. Soc.*, 1915; *J. Physiol.*, **49**, xxxii).—In centrifugalised blood the deeper layers of corpuscles are often darker in tint than those on the surface, but it was found that the percentage saturation with oxygen is the same throughout; the colour of the blood in reflected light is therefore not simply a function of the oxygen content. W. D. H.

The Action of Carbon Dioxide on the Blood Pressure. E. P. CATHCART and G. H. CLARK (*J. Physiol.*, 1915, **49**, 301—309).—The active substance that causes a rise of arterial pressure when carbon dioxide is administered to an intact animal is adrenaline. Its secretion can be prevented, and the rise of pressure eliminated by *apo*codeine or nicotine. Carbon dioxide produces no rise in blood pressure when anæsthesia is deep or the animal decapitated. The effect on the suprarenals is therefore excited through the agency of some mechanism in the central nervous system. W. D. H.

Significance of the Hydrogen-Ion Concentration of the Blood and Tissues. L. MICHAELIS (*Chem. Zentr.*, 1915, i, 1004—1005; from *Deutsch. med. Woch.*, **4**, 1170—1171).—For most biological purposes the hydrogen-ion concentration is the most useful expression of the reaction of a solution, since the activity of the enzymes is dependent on this factor. The hydrogen-ion concentration of the blood is essentially conditioned by the relative amounts of carbon dioxide and sodium carbonate which it contains, being given by the factor $3 \times 10^{-7} \times [CO_2]/[NaHCO_3]$. This has a value of $0{\cdot}45 \times 10^{-7}$, that is, the blood is distinctly alkaline, and this slight alkalinity is maintained by the organism by means of the lungs (expulsion of carbon dioxide) and the kidneys (deposition of acid or alkaline phosphates). The reaction of the juices of the tissues is almost exactly neutral. G. F. M.

Changes in the Alkalinity of Blood during Digestion. DONALD D. VAN SLYKE, GLENN E. CULLEN, and EDGAR STILLMAN (*Proc. Soc. expt. Biol. Med., New York*, 1915, **12**, 184).—The reserve alkalinity (indicated by the amount of carbon dioxide with which it can combine) of the plasma increases during digestion, and the alveolar carbon dioxide rises simultaneously; this is the result of secretion of the gastric acid, and absorption of alkaline digestion products. W. D. H.

Vividiffusion Experiments on the Ammonia of the Circulating Blood. ALICE ROHDE (*J. Biol. Chem.*, 1915, **21**, 325—330).—Shed blood kept aseptically liberates ammonia, as Medvedev states.

In a dialysate obtained from circulating blood by the vividiffusion method, the liberation of ammonia is very slight, and the ammonia in it equals that of the circulating blood. The source of the slowly liberated ammonia is in the non-dialysable constituents of the blood.
W. D. H.

The Oxidising Power of Oxyhæmoglobin and Red Corpuscles. J. F. McClendon (*J. Biol. Chem.*, 1915, **21**, 275—281).—A full account of work of which preliminary accounts have already appeared (this vol., i, 182, 185). W. D. H.

The Relationship of Creatinuria to Changes in the Sugar Content of the Blood. William MacAdam (*Biochem. J.*, 1915, **9**, 229—239).—After the injection of hydrazine in rabbits, if no alteration in the sugar-content of the blood occurs, there is no marked creatinuria; the excretion of creatine is associated with a state of hyperglycæmia. Creatinuria is not dependent on starvation *per se*, for in two fasting experiments hyperglycæmia also occurred. It is one of the earliest and most sensitive manifestations of a disturbance in the equilibrium of carbohydrate metabolism. W. D. H.

The Influence of Salicylates on the Uric Acid Concentration of the Blood. Morris S. Fine and Arthur F. Chace (*J. Biol. Chem.*, 1915, **21**, 371—375).—A full account of a research, of which a preliminary notice has already appeared (this vol., i, 339).
W. D. H.

Estimation of Glyoxalase in the Blood. Harold Ward Dudley (*Biochem. J.*, 1915, **9**, 253—259).—Glyoxalase is estimated from the amount of *l*-mandelic acid formed from phenylglyoxal hydrate; full details are given. The amount in the blood varies in different species, but is constant in animals of the same species; a high glyoxalase value indicates high tolerance for sugar.
W. D. H.

Coagulation Time of Blood. VII. Influence of Anæsthetics. Walter L. Mendenhall (*Amer. J. Physiol.*, 1915, **38**, 33—51).—Chloral hydrate and chloroform do not alter the coagulation time unless it is normally short; then it is prolonged. The effect is probably due to interaction between two or more organs, namely, the adrenal gland and liver (or intestine?). No retarding agent is produced. Ether-anæsthesia hastens coagulation wholly through its action on the adrenals. W. D. H.

Coagulation in Relation to the Proteins of the Blood. Alfred J. Hess and E. J. Banzhaf (*Proc. Soc. expt. Biol. Med., New York*, 1915, **12**, 198—199).—During immunisation the globulins of the blood increase and the albumins diminish. This, however, makes no change in the coagulation rate. W. D. H.

The Kjeldahl Method in Serological Work. Byron W. Barshinger (*Proc. Soc. expt. Biol. Med., New York*, 1915, **12**, 197).—The nitrogen in serum is unchanged at whatever temperature it is separated. If allowed to remain in contact with the clot, the nitrogen may increase 100%. Variations as great as 40% may be observed in samples removed from the same rabbit at the same bleeding, and in the sera of normal rabbits of the same age, size, breed, and diet. W. D. H.

The Fermentative Activity of the Blood and Tissues after Extirpation of the Pancreas. II. Nuclease. V. Stavraki (*Biochem. Zeitsch.*, 1915, **69**, 363—369).—The nucleolytic activity was investigated by determining the changes in the rotation of a 2% sodium nucleate (from yeast) solution produced by incubation for twenty-four hours with serum or extracts of organs. The depancreatisation of dogs was found in all cases to produce a marked decrease in the nuclease content of serum and extracts of organs. S. B. S.

The Fermentative Activity of the Blood and Tissues after Extirpation of the Pancreas. III. Diastase. V. Stavraki (*Biochem. Zeitsch.*, 1915, **69**, 370—388).—There is a marked decrease in the amylolytic action of the serum and of organ extracts of a dog after depancreatisation, which is found twenty-four to forty-eight hours after the operation. In the sixth to the ninth day there is again a small rise in the amylase content in the blood; the amylase never, however, disappears entirely. The amylolytic action of the salivary glands and kidneys is not diminished less than that of the other organs by removal of the pancreas. This also causes marked diminution of the liver amylase; there is no justification, however, for regarding this organ as the source of the diastatic ferments, for even in the first days after the operation there is a large amount of fat infiltration, and a consequent depression of the functions of the cells. Depancreatisation produces a marked increase in the amylolytic action of the rump muscles, which can be detected even twenty days after the operation, if the animals live so long. Decrease of the amylolytic action of the blood is not affected by the entrance of bile into this fluid. S. B. S.

The Free Amino-nitrogen of the Proteins of Ox and Horse Serum. Percival Hartley (*Biochem. J.*, 1915, **9**, 269—271).—The free amino-nitrogen of these proteins is equal to one-half of the lysine nitrogen; this confirms the results of van Slyke and Birchard (A., 1914, i, 212). W. D. H.

Chemical Differences in the Serum of Old and Young Rats. A. S. Grünbaum, H. G. Grünbaum, and H. S. Raper (*Proc. Physiol. Soc.*, 1915; *J. Physiol.*, **49**, xxviii).—The phosphative content of the serum in young rats is almost double that of adults; the inactivated serum of young rats assists cobra venom hæmolysis much more than that of adults. This parallelism does not seem to obtain in other

species. Young rats are, further, more susceptible to inoculated sarcoma, and to certain infections. W. D. H.

Inhibition of Sodium Oleate Hæmolysis and Toxicity by Cholesterol. Oskar Klotz and May E. Bothwell (*Proc. Soc. expt. Biol. Med., New York*, 1915, **12**, 199—201).—The hæmolytic and toxic effects of intravenously injecting sodium oleate can be prevented by mixing with it an equal quantity of cholesterol. In this combination a means is further provided of introducing cholesterol in a fluid state which is assimilable. W. D. H.

Basal Metabolism and Body Surface. James H. Means (*J. Biol. Chem.*, 1915, **21**, 263—268).—Observations on sixteen normal persons indicate that Du Bois' formula gives figures which deviate less from the average metabolism than Meeh's formula. The former formula may serve as a basis for detecting fundamental changes in metabolism, and cases of hypo- or hyper-thyroidism lie without the normal zone. W. D. H.

Influence of Fat and Carbohydrate, in Protein Hunger, on Nitrogen Secretion. Heinrich Zeller (*Chem. Zentr.*, 1914, ii, 650—651; from *Arch. Anat. Phys.*, 1914, 213—236).—The results of experiments with dogs and human subjects showed that 70—90% of carbohydrates may be replaced by isodynamic amounts of fat without exceeding the minimum nitrogen secretion obtained with exclusively carbohydrate food. For the complete combustion of the fat the food must contain at least one part of carbohydrate to four parts of fat. The carbamide nitrogen can be reduced to 40% of the total. The elimination of creatine and creatinine is the same with pure carbohydrate food and fat.

The amounts of uric acid and purine diminish at the beginning of the period with pure fat; later on, even with abundance of sugar, the amounts rose above the values obtained in the sugar period. The increased elimination of nitrogen resulting from consumption of pure fat seems to be due to increased decomposition of proteins. N. H. J. M.

The Metabolism of Creatine and Creatinine. VII. The Fate of Creatine when Administered to Man. Victor C. Myers and Morris S. Fine (*J. Biol. Chem.*, 1915, **21**, 377—381).—At most between 1·5 and 2% of the creatine given is excreted as creatinine. W. D. H.

The Smallest Quantities of Some Odoriferous Substances Perceptible to a Dog. Lorenz Seffrin (*Zeitsch. Biol.*, 1915, **65**, 493—512).—The author has ascertained what are the smallest quantities of various perfumes and other substances which, when mixed with 500 c.c. of air and inhaled by a dog through the nose, evoke the sniffing reflex. These quantities, expressed in c.c., are termed "perceptible minima," and, in the first group of substances investigated, range from 0·0005 for anisaldehyde to 0·01 for rose

oil, the intermediate substances, arranged in order, being xylene, toluene, amyl benzoate, ethyl ether, formaldehyde, methyl salicylate, safrole, jasmine, narcissus, neoviolon, and vanillin. In the case of most of these substances, man's sense of smell is found to be about twice as keen as the dog's. With the second group of substances, which were of animal origin and included the blood and urine of a dog and the muscle juices of various animals, the dog greatly surpassed the man in his perceptive power. The "perceptible minimum" for these materials in the case of the dog is of the order of 0·002 gram per 500 c.c. of air, whereas quantities a hundred times as large are not capable of stimulating the human olfactory mucous membrane. H. W. B.

The Formation of Fats from Proteins in the Eggs of Fish and Amphibians. J. F. McClendon (*J. Biol. Chem.*, 1915, **21**, 269—274).—During the development of the *Cryptobranchus* (Giant Salamander) egg there is an increase of about 8% in the higher fatty acids; in the egg of the brook trout the increase is 5·6%.

In these eggs vitallin is the chief reserve material, and it is probable that this is transformed into fatty and other substances. W. D. H.

The Inhibitory Effect of Adrenaline on the Sphincter of the Pupil. Don R. Joseph (*Proc. Soc. expt. Biol. Med., New York*, 1915, **12**, 212).—Adrenaline produces without exception a relaxation of this sphincter in cattle, sheep, and hogs. The sphincter is still irritable, for physostigmine produced a good contraction. This indicates that the cervical sympathetic nerve supplies inhibitory fibres to the sphincter muscle of the iris. W. D. H.

Tissue Fibrinolysins. Meyer S. Fleisher and Leo Loeb (*J. Biol. Chem.*, 1915, **21**, 477—501).—Certain organs, especially of the genito-urinary and nervous systems, contain fibrinolysins, which are destroyed by heating at 56° for thirty minutes. The fibrinolytic power differs in different species, and different kinds of blood vary in solubility. The effect is counteracted by the liver. The substances which inhibit blood coagulation may be identical with fibrinolysis; they inhibit growth, and thus antagonise tissue coagulins. They do not appear to be the same as the autolytic enzymes. W. D. H.

Influence of Di-iodotyrosine and Iodothyrin on the Secretion of Cerebro-spinal Fluid. Charles H. Frazier and Max Minor Peet (*Amer. J. Physiol.*, 1915, **38**, 93—97).—The authors have previously shown that thyroid extract slows the rate of secretion of cerebro-spinal fluid. The same depressant effect is obtained by the intravenous injection of di-iodotyrosine, but it is less marked than that obtained by injection of saline extracts of the fresh gland; iodothyrin causes the same effect, but very feebly. W. D. H.

Chemistry of Nerve. II. Estimation of Phosphorus in the Ventral and Dorsal Medullary Fibres of the Ox. G. Buglia and D. Maestrini (*Chem. Zentr.*, 1915, i, 376; from *Arch. Farm. sperim.*, 1914, **18**, 221—224).—The phosphorus present in the dorsal and

ventral medullary fibres is mainly organic phosphorus and chiefly phosphatide phosphorus (soluble in ether). The total phosphorus of the dorsal fibres is uniformly greater than that of the ventral. The difference persists in the dry material, and cannot be attributed, therefore, to a difference in the water or inorganic content. Phosphatide phosphorus is approximately the same for each variety, but phosphorus in other types of compound is present in greater quantity in the dorsal fibres. Whilst in the ventral fibres the difference between lipoid and organic phosphorus is scarcely noticeable, in the dorsal fibres it amounts to 3·5% of the total phosphorus. This points to the possibility that the dorsal fibres contain a small quantity of phosphorus in a special type of organic compound, in addition to the phosphatide phosphorus. H. W.

Chemistry of Nerve. III. Chemical Composition of the Ventral and Dorsal Medullary Fibres of the Ox. G. Buglia and D. Maestrini (*Chem. Zentr.*, 1915, i, 376; from *Arch. Farm. sperim.*, 1914, **18**, 271—275. Compare preceding abstract).—The previously noticed differences in the phosphorus and nitrogen content of the dorsal and ventral medullary fibres are not confined to the portion of these substances which can be extracted with alcohol and ether. The amount of material which can be extracted with physiological salt solution and coagulated by heat is greater in the case of the dorsal fibres, and this is connected with the difference in the total phosphorus and nitrogen content. H. W.

The Gaseous Metabolism and Efficiency of the Mammalian Heart. C. Lovatt Evans and Y. Matsuoka (*J. Physiol.*, 1915, **49**, 378—405).—In calculating the heart's work, the velocity factor must be allowed for when the work is high; it may account for 5% of the total work. Increase of arterial pressure, or increase of the heart's output, raises its gaseous metabolism up to a certain limit, beyond which diminution occurs. Increase of output is more economically performed. The maximal mechanical efficiency is about 20%, and is obtained by a moderate increase, both in pressure and output. Cardiac dilatation is accompanied by lower efficiency and fatigue. There is usually parallelism between the oxygen usage and the heart's volume. W. D. H.

The Effect of Adrenaline on the Heart-Rate. Walter J. Meek and J. A. E. Eyster (*Amer. J. Physiol.*, 1915, **38**, 62—66).—Intravenous injection of physiological amounts of adrenaline in unanæsthetised dogs with good vagal tone decreases the heart-rate, which is the net result of two effects, namely, acceleration of the heart directly, and reflex inhibition through the vagus. The cardiac acceleration due to moderate exercise can, therefore, scarcely be due to secretion of adrenaline, although this is a probable factor in extreme muscular exertion when vagal tone is diminished. As usual, therefore, adrenaline exercises a stimulating effect in times of physiological need. W. D. H.

Chemical Changes in the Bile produced by the Action of Substances Toxic to the Liver, and their Relationships to the Pathogenesis of Gall-stone Diseases. LUIGI D'AMATO (*Biochem. Zeitsch.*, 1915, **69**, 353—362).—Experiments were carried out on dogs with biliary fistulæ, and the effect was ascertained of the injection of various toxic substances on the bile secreted. The substances employed were ethyl alcohol, a mixture of amyl and ethyl alcohols, butyric acid, and cultures of *B. coli*. The general result of the toxic action was to produce a marked increase in the nucleo-proteins (five-fold or even more), and a marked diminution in the bile-salts, whereas the free and combined cholesterol diminish only slightly. The author regards the chemical conditions as favourable for the separation of cholesterol and the formation of gall-stones. S. B. S.

The Excretion of Sugars by the Kidney. GEORGE PEIRCE and NORMAN H. KEITH (*Proc. Soc. expt. Biol. Med., New York*, 1915, **12**, 210—211).—The kidney uses a relatively large amount of oxygen, and probably this is employed in the oxidation of dextrose, the main source of the body's energy. The sugar normally gets into the kidney cells from the blood in proportion to its concentration there; during its passage it is oxidised, and if the amount is normal it is all oxidised, so that practically none gets as far as the urine. When this threshold is passed, glycosuria results. It is only those sugars which are oxidisable in the body which show this threshold phenomenon. W. D. H.

Synthesis of Hippuric Acid in Nephrectomised Dogs. F. B. KINGSBURY and E. T. BELL (*J. Biol. Chem.*, 1915, **21**, 297—301. Compare this vol., i, 104).—Considerable amounts of hippuric acid are found in blood and tissues after removal of the kidneys. The kidneys are therefore not the only organs which form this substance. W. D. H.

Influence of Alkalis on the Function of the Pancreas Glands. V. N. VAROBÉEV (*Chem. Zentr.*, 1914, ii, 1280).—Intravenous injection of alkalis (Na, K, Li, NH_3, Ca, Mg, in different compounds) causes an increased secretion of the pancreatic juice. With alkalis which are readily soluble in water, the action is rapid, but transient; less soluble alkalis cause a slower but more lasting action in dilute solution, whilst more concentrated solutions restrict the activity of the glands. H. W.

Composition and Physiological Activity of the Pituitary Body. FREDERIC FENGER (*J. Biol. Chem.*, 1915, **21**, 283—288).—The proportionate size of the posterior lobe is twice as great in the pig as in cattle; but the physiological action on the uterus is the same. No seasonal variations were noted in cattle. About 10% of the ox-gland contains colloid masses between the two lobes. This material is insoluble in acidified water, and does not possess any pronounced power to make the uterus contract. W. D. H.

Pituitary Secretion. Douglas Cow (*J. Physiol.*, 1915, **49**, 367—377).—This secretion is increased by duodenal extracts; the products of activity are excreted into the cerebro-spinal fluid, and when the secretion is increased, can be recognised there by the usual physiological tests. W. D. H.

The Metabolism of Creatine and Creatinine. VIII. The Presence of Creatinine in Muscle. Victor C. Myers and Morris S. Fine (*J. Biol. Chem.*, 1915, **21**, 383—387).—Muscle does undoubtedly contain creatinine, and the content in this tissue is higher than in the blood or the other tissues. The urinary creatinine is believed to originate mainly in the muscular tissues. Full analytical details are given. W. D. H.

The Metabolism of Creatine and Creatinine. IX. The Creatine Content of the Muscle of Rats Fed on Isolated Proteins. Victor C. Myers and Morris S. Fine (*J. Biol. Chem.*, 1915, **21**, 389—393).—The creatine content of rats' muscle remains very constant under the dietary conditions imposed. A high or low content of arginine in the proteins given exerts no marked influence.

On a diet of caseinogen (poor in arginine) the creatine content of the muscle is about 2·5% below that on an edestin diet.

W. D. H.

Distribution of Phosphorus in Striated Muscle. A. E. Rabbeno (*Chem. Zentr.*, 1915, i, 323; from *Arch. Farm. sperim.*, 1914, **18**, 9—36, 49—65).—The author has determined the total, phosphatide, inorganic, and nuclein-phosphorus in normal and in atrophied human muscle, and in the muscle of a normal and a fasting dog. Phosphatide-phosphorus was extracted with light petroleum and ether, and the inorganic phosphorus removed from the phosphatide-free residue by means of dilute acid; the nuclein-phosphorus was estimated in the residue obtained in this manner. Inorganic phosphorus forms 65% of the total phosphorus. The greater portion of the organic phosphorus is nuclein phosphorus. In the different experiments only small variations in the distribution of phosphorus were noticed. H. W.

Chemistry of Muscle. VI. Organic Phosphorus contained in the Non-striated Muscle of Mammals. A. Costantino (*Chem. Zentr.*, 1915, i, 486; from *Arch. Farm. sperim.*, 1914, **18**, 396—403).—The non-striated muscle of the ox (*retractor penis*) contains a large quantity of protein phosphorus, amounting approximately to ten times that present in the nucleoproteins of striated muscle.

H. W.

Chemistry of Muscle. VII. Changes of the Different Substances containing Phosphorus in the Non-striated Muscle of Mammals during the Autolytic Processes. A. Costantino (*Chem. Zentr.*, 1915, i, 486; from *Arch. Farm. sperim.*, 1914, **18**, 425—433. Compare preceding abstract).—During autolysis of the non-striated muscle (*retractor penis*), under the influence of ferments,

a considerable increase in the phosphorus soluble in water, particularly of inorganic phosphorus, is observed. Proteins containing phosphorus (nucleoproteins, phosphoproteins) appear to undergo decomposition, yielding soluble phosphorus compounds, whilst the phosphatides are only hydrolysed to an unimportant extent.

H. W.

Chemistry of Muscle. VIII. Organic Phosphorus and Constituents of the Ash of the Non-striated Muscle of Mammals. A. COSTANTINO (*Chem. Zentr.*, 1915, **i**, 486—487; from *Arch. Farm. sperim.*, 1914, **18**, 480—485. Compare preceding abstracts).—The phosphatides of non-striated muscle can be completely extracted with 95% alcohol. The fatty acids contained in these phosphatides comprise about 80% of the total higher fatty acids of non-striated muscle. About 75% of that portion of the alcoholic extract which is soluble in ether–acetone consists of unsaponifiable matter.

The ash from non-striated muscle has a smaller iron (0·002%) and magnesium (0·0122%) content than that from striated muscle.

H. W.

Behaviour of Organic Fats during Autolysis. II. Liberation of Fat and Autolytic Proteolysis in Muscle. LEONE LATTES (*Chem. Zentr.*, 1915, **i**, 487; from *Arch. Farm. sperim.*, 1914, **18**, 335—341).—Estimation of free and of combined fat, and of total and of amino-nitrogen in muscle which has been subjected to prolonged sterile autolysis shows that, at a certain period in the autolysis, fat is liberated from a compound which is insoluble in ether. During autolysis a gradual increase in the ammonia and amine-nitrogen is observed, which, after a relatively long interval, leads to such values as are rapidly attained by putrefaction. A parallelism exists between the proteolysis and the liberation of fat, but it is not impossible that the latter is to be attributed to the fission of a complex protein.

H. W.

Chemistry of Echinoderms. A. KOSSEL and S. EDLBACHER (*Zeitsch. physiol. Chem.*, 1915, **94**, 264—283).—From the testicle of *Astropecten aurantiacus* a histon is extracted by dilute sulphuric acid which contains 10·9% of arginine, 10·8% of lysine, and some tyrosine, but no histidine, tryptophan, or cystine. Similar histons are present in a free state in the testicles of *Echinus acutus* and *Strongylocentrotus lividus*.

Taurine is present in a free state in the testicles, ovary, and cæcum of *Astropecten*, and is extracted by alcohol. Glycine, *iso*leucine, sarcosine, tyrosine, and glutamic acid are also found in the alcoholic extract of the testicle of *Astropecten*. The testicle of *Strongylocentrotus* contains glycine, but no taurine.

A new sterol, *stellasterol*, $C_{27}H_{44}O$, has been obtained from the testicle and cæcum of *Astropecten*. It has m. p. 149—150°, and closely resembles cholesterol in solubility and general properties. It does not, however, give a typical Salkowski reaction with chloro-

form and sulphuric acid. Treatment with acetic anhydride gives the *acetate*, $C_{29}H_{46}O_2$, rhombic plates, m. p. 176—177°. The *benzoate* melts first at 100°, forming a cloudy, opalescent liquid, which then clears sharply at 125°.

From the alcohol-insoluble material of the cæcum of *Astropecten*, a substance is extracted with ether, which is termed *astrol*, $C_{23}H_{48}O_3$. It crystallises in the form of bent needles, m. p. 71°, and gives neither Liebermann's nor Salkowski's reactions.

H. W. B.

The Influence of Balanced and Non-balanced Salt Solutions on the Osmotic Pressure of the Body Liquids of Fundulus. JACQUES LOEB and HARDOLPH WASTENEYS (*J. Biol. Chem.*, 1915. **21**, 223—238).—This body-juice is affected more strongly by non-balanced than by balanced solutions, especially when the former is of pure sodium chloride. The non-balanced solutions increase the permeability of the cells. The effect is due to the toxic action of the salt on the gills, and the fish often dies before marked changes in osmotic pressure have taken place. Balanced solutions, such as sea-water, when concentrated, increase the osmotic pressure of the body-juice, possibly by at first increasing the permeability of gills and skin. In $M/2$-sea water the osmotic pressure falls, but feeding inhibits the decline.

W. D. H.

The Eosinophile Cell of Teleostean Fish. ALAN N. DRURY (*J. Physiol.*, 1915, **49**, 349—366).—Metchnikov objects to the view that these cells excrete a toxin for bacteria because they are absent in teleostean fish. They are, however, not absent, although they are much less stable than in mammals.

W. D. H.

The Relation of the Quality of Proteins to Milk Production. E. B. HART and G. C. HUMPHREY [with W. H. BENTLEY] (*J. Biol. Chem.*, 1915, **21**, 239—253).—Experiments with the proteins of milk, maize, and wheat show that the kind of protein is an important factor, and that the synthetic powers of the mammary gland will not compensate for deficiencies in protein-structure.

The milk proteins have an efficiency for milk production and tissue restoration of about 60, maize protein 40, and wheat protein 36%.

W. D. H.

The Reaction and Calcium Content of Milk in the Coagulation Process. THOMAS HUGH MILROY (*Biochem. J.*, 1915, **9**, 215—228).—During the action of rennin there is no change in the hydrogen-ion concentration. The addition of an alkali oxalate to milk lowers, whilst that of calcium chloride raises this concentration. Fresh milk which has been heated for an hour to near boiling point shows a rise in the hydrogen-ion concentration, and a fall in calcium content; rennin acts on it very slowly, but its coagulability may be increased by the addition of calcium chloride, or by raising the hydrogen-ion concentration. The acid precipitation zone of caseinogen lies on the acid side of the rennin zone of

action, but the latter gradually approaches the former as the calcium content is lowered. Calcium chloride, apart from its effect on the hydrogen-ion concentration, increases the activity of rennin from the beginning of the digestion process. W. D. H.

Cases of Low Level of Nitrogen Excretion. J. HOLKER, J. P. SCOTT, and F. W. LAMB (*Proc. Physiol. Soc.*, 1915; *J. Physiol.*, **49**, xxiii).—Two cases are recorded without comment; both were females between thirty and forty years of age; one lived a sedentary life and excreted on the average 3·86 grams of nitrogen, the other of about the same weight led an active life, and excreted on the average 5·86 grams of nitrogen daily. In both cases urea was the most abundant nitrogeneous substance (3·25 and 4·63 grams per diem respectively). No details of diet are given. W. D. H.

Influence of Fat and Carbohydrate with Abstinence from Protein on the Secretion of Neutral Sulphur in the Urine. HEINRICH ZELLER and HANS STRACZEWSKI (*Chem. Zentr.*, 1915, i, 1074).—When the carbohydrates in a protein-free diet are replaced entirely by fat, the excretion of neutral sulphur increases with that of the nitrogen, and it seems probable, therefore, that during the fat period more protein is decomposed. A comparison of the excretion of neutral sulphur in the case of dogs, that were sometimes fed on fat and other times on carbohydrate, showed no increased secretion when bromobenzene was administered as well, but in the absence of bromobenzene much more neutral sulphur appeared in the urine with the fat than with the carbohydrate diet. The protein metabolism is therefore disturbed by the bromobenzene and its derivatives formed in the body, as also by the fat diet in the absence of carbohydrate and protein, although it does not follow that the cause and nature of this disturbance are the same. G. F. M.

Effect of Various Foods on the Occurrence of Methyl Alcohol in Urine. TH. VON FELLENBERG (*Chem. Zentr.*, 1915, i, 752—753; from *Mitt. Lebensmitteluntersuch. und Hyg.*, **6**, 24—27).—The pectin introduced into the system by vegetable and fruit diet gives rise to 9—12% of its weight of methyl alcohol. This has no poisonous action because in normal circumstances it is probably almost entirely oxidised in the body. Small quantities are excreted in the urine, but with an exclusive fruit diet the amount is less than 1%. The methyl alcohol is liberated, not only by the action of pectase, but also by the digestive juices of the body, and it is therefore immaterial whether fruit and vegetables are eaten raw or whether the pectase is destroyed by cooking. The quantity of methyl alcohol excreted is increased by taking ethyl alcohol in the form of wine or beer along with substances containing pectin, as its presence retards the combustion of methyl alcohol in the body. Whilst, therefore, the eating of even large quantities of fruit will never lead to methyl alcohol poisoning, the consumption of spirits containing comparatively large quantities of methyl alcohol is distinctly dangerous. G. F. M.

The Synthesis of Hippuric Acid in the Animal Organism and the Occurrence of Benzoic Acid in the Urine. G. W. RAIZISS and H. DUBIN (*J. Biol. Chem.*, 1915, **21**, 331—343).—The synthesis of hippuric acid in rabbits is quantitative when no more than 1 gram of benzoic acid per kilo. of body-weight is given. With larger doses on a vegetable diet, the synthesis ranges from 80 to 90%, and the rest of the benzoic acid appears in the urine. On a milk and egg diet, synthesis is favoured (96%), and the ability to synthesise increases after repeated doses. The largest amount of the free acid appears within six hours after feeding. In order to estimate benzoic acid in the presence of hippuric acid, the urine should be collected in dilute nitric acid. W. D. H.

Elimination of Salicyluric Acid and Salicylic Acid after Administration of Salicylic Acid, Sodium Salicylate, and Diplosal. ALESSANDRO BALDONI (*Chem. Zentr.*, 1915, i, 324; from *Arch. Farm. sperim.*, 1914, **18**, 151—177).—Estimations of salicyluric and salicylic acids in human urine after administration of the above-named drugs have been effected by the method described previously. The bulk of the salicylic acid administered appears to combine with glycine, and to be eliminated as salicyluric acid. The ratio of combined to free salicylic acid varies with different persons, and, even with the same individual, does not appear to be constant under apparently uniform conditions. The synthetic formation of salicyluric acid is not noticeably influenced by the simultaneous administration of benzoic acid and the consequent production of hippuric acid. H. W.

Salt and Diuretin Hyperglycæmias. ERNST HIRSCH (*Zeitsch. physiol. Chem.*, 1915, **94**. 227—263).—Intravenous injection of physiological salt solution (0·85% sodium chloride) into a rabbit does not lead to any marked hyperglycæmia provided the animal is free from restraint. Hyperglycæmia may set in if the animal is bound or operated on before any injection of the salt solution has taken place; and after this preliminary hyperglycæmia has subsided, injection of physiological salt solution does not increase the amount of sugar in the blood beyond 0·19%, and glycosuria is not produced. Even salt solution of 2·5% strength does not produce hyperglycæmia or glycosuria.

Intravenous injection of 10% sodium chloride solution into rabbits is regularly followed by hyperglycæmia and glycosuria; but 2% and 2·5% sodium carbonate, 1% and 2% sodium acetate, and 1% calcium chloride solutions are ineffective. Intravenous injection of small quantities of 1% magnesium sulphate solution, which produces narcosis and partial tissue asphyxiation, is accompanied by a rise in the content of sugar in the blood and the urine.

Subcutaneous and intravenous injection of diuretin invariably produces hyperglycæmia, and when the content of sugar in the blood reaches 0·27%, glycosuria supervenes. The glycosuria following salt or diuretin injections is due, not to an increased permeability of the kidney, but to the preceding hyperglycæmia.

The author draws special attention to the fact that restraining the movements of an animal or any slight operation may cause the onset of marked glycosuria. H. W. B.

Changes in the Fat Content of Fæces Measured by Freezing without the Addition of a Preservative. C. A. Smith, Raymond J. Miller, and Philip B. Hawk (*J. Biol. Chem.*, 1915, **21**, 395—401).—The fat of fæces kept at −12° shows a decrease, but the fatty acid increases owing to hydrolysis. Freezing alone is therefore not a trustworthy method. The Saxon method is commended. W. D. H.

Relation of Steric Atomic Grouping to Carcinoma. Ernst Freund and Gisa Kaminer (*Chem. Zentr.*, 1915, i, 1079; from *Wien. Klin. Wochenschr.*, **27**, 357—358).—Earlier experiments having shown that an organic substance of unknown structure extracted from the intestines exhibited a specific action towards carcinoma serum and carcinoma cells, the behaviour of certain substances of known structure was examined, and it was found that maleic, citraconic, ethylmalonic, dimethylmalonic, and malonic acids had the same specific action. Since compounds isomeric with these acids do not exhibit this action, it is assumed that a certain definite steric position of the two carboxyl groups is necessary for this specific pathological relationship to the carcinoma cells. Maleic acid shows a complete analogy to the intestinal acid in its action on serum, and also on dextrin solutions. G. F. M.

Ethylhydrocupreine Chemotherapy in Infectious Diseases. Arthur D. Hirschfelder and Frederic H. Schlutz (*Proc. Soc. expt. Biol. Med., New York*, 1915, **12**, 208).—This quinine derivative has prophylactic and curative powers in pneumococcus septicæmia in mice (Morgenroth). In the present work the hydrochloride shortened the duration of attacks of measles; but the effect in scarlet fever was negligible. Negative results were also obtained in rabies, vaccinia, and trachoma. W. D. H.

The Abderhalden Reaction. Helmuth Thar and Nina Kotschnev (*Biochem. Zeitsch.*, 1915, **69**, 389—402).—The investigations were carried out by estimating the amino-nitrogen in the dialysates. Placenta proteins are not degraded by normal human sera. The proteins of placenta, carcinoma, and lung are degraded by the sera of pregnant individuals. Placental protein is degraded by the sera of nephritic individuals. Brain proteins are not degraded by the sera of the insane. Carcinoma proteins are degraded by the sera of carcinomatous subjects. Even in the positive cases the ninhydrin reaction is negative, as the concentration of the reactive products is too low. Placental and lung proteins are degraded by the expressed juice of placenta, but not of the proteins of carcinomata. The authors call attention to the fact that their method is too complex for adaptation to clinical diagnosis. They claim that Abderhalden's optical method is of no use for distinguishing between the sera of normal and pregnant individuals. S. B. S.

Relation of Diet to Transmissible Tumours. J. E. Sweet, Ellen P. Corson-White, and G. J. Saxon (*J. Biol. Chem.*, 1915, **21**, 309—318).—Observations on tumour-bearing rats and mice confirm the authors' previous conclusion that tumour cells are subject to the same laws of growth as normal cells, the only difference being that the former possess a stronger avidity for the unknown substances in the diet which are essential for growth, and therefore they continue to grow, although the animal may lose weight. This unknown material might also originate from the breakdown of normal cells. W. D. H.

Destruction of Typhus Bacilli in the Organism of the Rabbit. II. Use of Halogen-substituted Aldehydes of the Methane Series. E. Hailer and W. Rimpau (*Chem. Zentr.*, 1915, i, 325; from *Arbb. Kais. Gesundh.-Amt.*, 1914, **47**, 291—297).—The possibility of chemotherapeutic influence on typhus infection of rabbits has been established by the experiments of Conradi with chloroform. The authors have attempted to use halogen-substituted hydrocarbons, which, in addition to being soluble, like chloroform, in lipoids, are to a marked extent soluble in water. For this purpose they have selected chloral hydrate, bromal hydrate, and butylchloral hydrate, the aldehydic nature of which renders a disinfecting action probable.

Chloral hydrate in vitro has only a slight germicidal action towards typhus bacilli; bromal hydrate has a more marked action, but butylchloral hydrate is the most powerful. Lipoid solubility and narcotic power are closely related to bactericidal action. Butylchloral hydrate, administered through the stomach, had a marked bactericidal effect on the typhus bacillus in an intravenously infected rabbit; when intravenously infected, it acted as a powerful poison. In some instances chloral hydrate influenced the degree of infection of the animals, but bromal hydrate was without action. H. W.

Destruction of the Typhus Bacillus in the Organism of the Rabbit. III, IV, and V. E. Hailer and E. Ungermann (*Chem. Zentr.*, 1915, i, 325—326; from *Arbb. Kais. Gesundh.-Amt.*, 1914, **47**, 303—346. Compare preceding abstract).—III. *Use of Mono- and Poly-hydric Phenols and Phenol Ethers.*—A number of members of the phenol series, both soluble and insoluble in water, have been examined with regard to their healing action towards rabbits infected with typhus. The following lipoid-soluble substances had a favourable action: *m*-xylenol, per os and per rectum; *m*-5-xylenol, per os; chloro-*m*-cresol, per os; β-naphthol, per os and intravenously; tribromo-β-naphthol, per os; hydroxyquinoline, per os; of the compounds soluble in water, pyrogallol alone was active. Carvacrol, phenetole, and anethole among lipoid-soluble substances, and the three dihydroxybenzenes among those soluble in water were inactive. A mixture of phenols, b. p. 230—240°, in contrast to one, b. p. 210—220°, proved noticeably active; hexamethylenetetramine

was inactive. The authors are led to the conclusion that it is quite possible to combat typhus in rabbits with substances which have also in vitro a bactericidal action.

IV. *Use of Aromatic Hydroxy-acids.*—The observation that the organs of rabbits infected with typhus became free from bacilli after intravenous injection of sodium salicylate solution has led the authors to examine the effect of homologues of salicylic acid. The results are summarised as follows: Administration of sodium salicylate solution per os caused the disappearance of typhus bacilli from the organs in one case out of five; intravenous injection had a similar action in five cases out of nine. *p*-Hydroxybenzoic acid, *o*-creosotic acid, phenoxyacetic acid, anisic acid, β-hydroxynaphthoic acid, and cinnamic acid were ineffective when used intravenously. *o*-Acetoxybenzoic and benzoic acids were each effective in one case of three, whilst β-hydroxynaphthoic acid caused freedom in one case in the organ examined.

V. *Use of Substances from the Group of Essential Oils.*—The investigation was undertaken because various essential oils are used for internal disinfection. The following substances were investigated: Borneol, terpin hydrate, linalool, terpineol, pinene, carvene, citronellaldehyde, carvone, cineole, camphor, camphoric acid, and certain vegetable oils. Conclusions as to the activity of definite groups cannot be deduced from the authors' results. Terpin hydrate and borneol, citronellaldehyde, carvone, and cineole had a marked action; the other substances were practically without effect.

H. W.

Destruction of Typhus Bacilli in the Organism of the Rabbit. VI. Treatment with Various Reagents of Rabbits Infected in the Gall Bladder. E. Hailer and G. Wolf (*Chem. Zentr.*, 1915, i, 385; from *Arbb. Kais. Gesundh.-Amt.*, 1914, **48**, 80—89. Compare preceding abstracts).—The experiments were undertaken because the infection caused in the manner indicated in the title exhibits close similarity to the infection in man. The following substances, the efficacy of which has been previously established, were employed: *m*-xylenol, thymol, pyrogallol, salicylic acid, sandel oil, pinene, cineole, and oil of cinnamon, in addition to *m*-hydroxybenzoic acid and salvarsan. Oil of cinnamon alone of these substances caused a disappearance of the typhus bacillus from the organism of the rabbit in isolated cases. H. W.

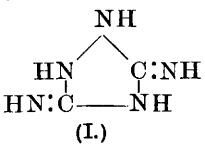
The Effect of Lead Salts and Nitrites on Intestinal Movements. A. D. Hirschfelder, J. M. Arnson, R. Honde, G. M. Merkert, and M. J. Shapiro (*Proc. Soc. expt. Biol. Med., New York*, 1915, **12**, 215—216).—Experiments on rabbits establish the rôle of nitrites as inhibitors of intestinal peristalsis, and furnish a basis for the therapeutic results of Riegel and Pal, who treated lead colic with amyl nitrite. These observers also used it in the gastric crises of tabes. The mechanism is not merely a change in blood pressure, but a direct action on the intestine. W. D. H.

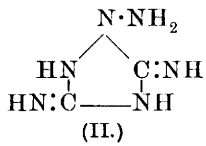
Physiological Action and Behaviour of Certain Derivatives of Benzene compared with those of *cyclo*Hexane. EDUARDO FILIPPI (*Chem. Zentr.*, 1915, i, 377—378; from *Arch. Farm. sperim.*, 1914, **18**, 178—192, 193—211).—The examination of toxicity, performed on rats, yielded the following results: Toluene, *p*-xylene, *cyclo*hexane, and *cyclo*hexanone caused cramp and paralysis of muscle. *o*- and *m*-Xylenes, mesitylene, benzyl alcohol, *cyclo*hexanol, 2-, 3-, and 4-methyl*cyclo*hexanols, methyl*cyclo*hexane, dimethyl-*cyclo*hexane, dimethyl*cyclo*hexanol, methyl-, dimethyl-, and trimethyl-*cyclo*hexanones have a sedative influence, in addition to which the last shows a distinct hypnotic action. All the substances investigated cause a decided hypothermia and a powerful vasodilatation.

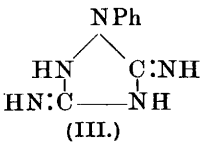
In the rabbit, *m*-xylene is oxidised to *m*-toluic acid, the formation of a xylenol being doubtful. *o*-Xylene is excreted as *o*-toluic acid. Mesitylene is oxidised to mesitylenic acid, and is mainly excreted as mesitylenuric acid; uvitic and trimesic acids are not formed. *cyclo*Hexane is mainly transformed into *cyclo*hexanone, a smaller portion being possibly converted into adipic acid; *cyclo*hexanone is degraded to adipic acid. The biological oxidations which have been observed are similar to the photochemical autoxidations studied by Ciamician and Silber with the same substances.

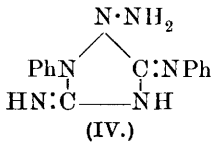
H. W.

Physiological Action of Guanazole and Certain Derivatives and their Behaviour in the Organism. GIOVANNI BATTISTA ZANDA (*Chem. Zeit.*, 1915, i, 323—324; from *Arch. Farm. sperim.*, 1914, **18**, 118—144, 145—150).—The author has investigated the action of guanazole (I), aminoguanazole (II), phenylguanazole (III), and diphenylaminoguanazole (IV) on guinea-pigs, mice, and frogs:


(I.)


(II.)


(III.)


(IV.)

The process of poisoning was the same in each case, but the toxicity increases considerably from I to IV. Only III and IV show a feeble bactericidal action, which is probably to be attributed to the phenyl group, and is therefore considerably more pronounced in IV than in III.

H. W.

α-Copper Gynocardinate (α-Cuprum Gynocardicum) and its Therapeutic Value for Tuberculosis and Leprosy. I. I. OSTROMISSLENSKI [and D. I. PETROV] (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 335—364).—Subcutaneous injection of α-copper gynocardinate

(this vol., i, 646) in solution in various solvents exerts a retarding influence on the course of tuberculosis in the porpoise, the life of the animal being considerably prolonged. A single injection of 0·01 or even 0·0065 gram of the salt has a marked effect. When administered to a healthy porpoise, it protects the latter from tuberculosis. It is not yet definitely settled whether a complete cure of an infected animal is possible in this way. It seems probable that this salt would have a similar influence in cases of leprosy, especially of the tubercular variety. The α-copper gynocardinate may be employed in 1% solution in a vegetable oil, such as olive oil, almond oil, camphor oil containing 10% of camphor, etc., or in 1—5% solution in vasogen, or in 1—4% solution in methyl gynocardinate. Opalescent, turbid, or supersaturated solutions of the salt should be avoided, and the preparation should be freshly made and sterilised at 130—150°. The injection of dilute (1—2%) solutions is to be preferred to that of concentrated (4—5%) ones. Intravenous injection is of no avail. T. H. P.

Comparative Activity of Compounds of Hexamethylenetetramine. H. Boruttau (*Chem. Zentr.*, 1914, ii, 1279).—The antiseptic action of hexamethylenetetramine towards urine can be greatly increased by combining it with an antiseptic such as salicylic, phthalic, or camphoric acid. The compound with boric acid is only slightly more active than the free base, but, on the other hand, the salts formed with anhydromethylcitric acid or citric acid show greatly enhanced activity. As far as the solution of the uric acid by urine is concerned, the author finds an increased action to be obtained by combining the base with citric, boric, borocitric, or phthalocitric acids, and, to a less extent, with sulphosalicylic acid. One molecule of the base is used for each molecule of acid. H. W.

Alterations in the Composition of the Blood and Brain Resulting from the Chronic Use of Narcotics. Ernst Waser (*Zeitsch. physiol. Chem.*, 1915, **94**, 191—204).—The blood and brains of dogs receiving daily doses of (1) paraldehyde, (2) veronal, and (3) chloral hydrate have, after several months' treatment, been compared with the blood and brains of normal animals, especially in relation to their content of fat, cholesterol, and phosphatides.

Paraldehyde appears to prevent the fatty degeneration of the brain which occurs with both of the other drugs employed, but it has an irritating action on the gastric mucous membrane, which results in an impaired general nutrition of the animal organism. Normal growth occurred to the greatest extent in the dog receiving chloral hydrate, but subsidiary toxic effects produced by the drug necessitated the premature death of the animal. Of the three drugs, veronal, in spite of considerable alterations produced in the cholesterol content of the blood and the brain, appears to be the best narcotic for chronic use, because it causes the least disturbance in the general condition of the animal. H. W. B.

Phenylacetylglutamine and its Formation in the Animal Body after Ingestion of Phenylacetic Acid. H. THIERFELDER and C. P. SHERWIN (*Zeitsch. physiol. Chem.*, 1915, **94**, 1—9. Compare this vol., i, 481).—Phenylacetylglutamine has been synthesised by the authors by the action of phenylacetyl chloride on glutamine, and found to be identical with the substance previously isolated from the urine (*loc. cit.*). It has $[\alpha]_D^{17} - 17{\cdot}9°$. Phenylacetylglutamine-carbamide has the rotation $[\alpha]_D^{15} - 14{\cdot}14°$.

Phenylacetylglutamic acid is prepared from *d*-glutamic acid and phenylacetyl chloride. It crystallises in microscopic needles, m. p. 123°, $[\alpha]_D^{18} - 19{\cdot}16°$, and gives a crystalline *brucine* salt.

Ingestion of 4·5 grams of phenylacetylglutamic acid does not lead to the appearance of phenylacetylglutamine in the urine, only traces of the unaltered acid being recovered. Phenylacetylglutamine is similarly eliminated in an unchanged condition by the animal organism. Since phenylacetylglutamic acid in recognisable quantity is produced when as little as 1 gram of phenylacetic acid is taken, it is probable that the glutamine component is a product of protein katabolism, and therefore normally present as such in the protein molecule. H. W. B.

Chemical Constitution and Physiological Action of Strychnine [Supposed Action of the Group ·N:CO· in the Strychnine Molecule in the Causation of Cramp]. CESARE PADERI (*Chem. Zentr.*, 1915, i, 323; from *Arch. Farm. sperim.*, 1914, **18**, 66—87).—Piperidone and pyrrolidone, which, like strychnine, contain the group :N·CO·, cause cramp, thus leading to the possible assumption that the latter property is attributable to this particular group. The author shows this hypothesis to be incorrect, since, on the one hand, pyridone and pyrazolone which contain the :N·CO· group do not give rise to cramp, whilst, on the other hand, strychnol in which this group is not present shows typical strychnine action. In a special series of experiments it is shown that the strychnol functions as such, and is not converted into strychnine within the organism. H. W.

Detection and Concentration of Antigens by Ultrafiltration and Pressure Dialysis with Special Reference to Diphtheria and Tetanus Toxins. ALEXANDER THOMAS GLENNY and GEORGE STANLEY WALPOLE (*Biochem. J.*, 1915, **9**, 298—308).—No antigen passes the collodion membranes described (this vol., ii, 549); the antigen may be thus obtained in a concentrated state, examined, and its nature determined. Mallein and tuberculin may be freed from glycerol in this way. The periodic recurrence of low-value toxins need no longer be feared. If ultrafiltration is followed by pressure dialysis, tetanus toxin may not only be concentrated, but freed from the disintegration products of broth materials, which are specially noxious. These membranes are impermeable to enzymes, but allow pituitrin, the co-enzyme of zymase, and the toxic constituent of Witte's peptone to pass. W. D. H.

Toxins and Antitoxins. I. Partial Synthesis of Antitoxins. I. I. Ostromisslenski (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 263—300).—From a consideration of the nature of toxins, antitoxins, and the compounds they form one with the other, of the mechanism of their actions, and of the specificity of antitoxins, the author draws the following general conclusions. In the majority of cases toxins are nitrogenous compounds of high molecular weight, and they exhibit a slightly basic character and colloidal properties. When introduced into the animal organism, they cause specific diseases, but their salts, unlike those of alkalcids and crystalline poisons, are generally non-poisonous. All antitoxins are globulins, which exhibit the ability to adsorb, in normal conditions, the corresponding toxins, but not other toxins. The interaction of toxins and antitoxins proceeds in three phases: (1) mutual adsorption, or, more generally, physical approximation of the toxin and antitoxin, the poisonous character of the former not being changed; (2) a chemical reaction or neutralisation, the toxin and antitoxin forming a non-poisonous, salt-like compound, resolvable by the action of acid or alkali; (3) profound chemical change of this compound, proceeding either intramolecularly or conditioned by the influence of the molecules of the surrounding medium, the resultant product not being decomposed into its constituents by acid or alkali. The specificity of an antitoxin is determined by the physical conditions of its colloidal particles, such as their surface, magnitude, mass, electrical state, and possibly the configuration of their molecules or the number of the latter in the colloidal particle. Only the physical condition of an antitoxin distinguishes it from normal globulins, which are passive towards all toxins, without exception. The process of the biological neutralisation of a toxin by an antitoxin may be represented chemically as the neutralisation of a weak organic base by a weak organic acid of amphoteric character.

The combination of the globulin with the toxin is only in rare cases brought about by heat alone. Thus, if staphylolysin, the toxin of pathogenic *Staphylococci*, is heated with rabbit serum at 60° for some hours, the globulin undergoes conversion into the antitoxin of staphylolysin. In other cases, the presence of a catalyst is necessary for this reaction. Sodium chloride has been used for this purpose, and with its help one and the same normal horse serum has been converted into the antitoxin of diphtheria and also into that of botulismus ("meat-poisoning"), the globulin–toxin compound being decomposed by acidification of the solution. The serum used may be replaced by a solution of the globulin isolated in the ordinary way, by the globulins of hens' eggs, etc., without affecting the properties of the antitoxins obtained.

T. H. P.

Toxins and Antitoxins. II. Transformation of Protein Substances into Specific Antitoxins. I. I. Ostromisslenski and D. I. Petrov (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 301—307. Compare preceding abstract).—The formation of bacterial toxins

during the growth of the organisms in a liquid medium is slow and progressive, the maximum concentration of toxin being reached only after some days or possibly months from the time of inoculation. It might, therefore, be expected that, in a medium containing a globulin, the molecules of nascent toxin would be adsorbed by the globulin. Experiments with horse serum and with Löffler's bacillus and *Bacillus botulinus* show that such adsorption actually does occur, but is not complete, part only of the toxin being converted into the corresponding antitoxin, whilst, in spite of the presence of excess of globulin, the rest of the toxin remains free. This limitation of the reaction is doubtless to be explained by the alkaline reaction of the nutrient medium, but neutralisation of the serum prevents the development of both the above organisms.

T. H. P.

Toxins and Antitoxins. III. Danysz Phenomenon. I. I. Ostromisslenski (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 307—313. Compare preceding abstracts).—Denysz (A., 1902, ii, 575) observed that when a toxin is added, not all at once, but in portions at intervals, to an equivalent quantity of an antitoxin, the toxin is not completely neutralised, the mixture remaining poisonous. Various explanations, none of which is perfectly satisfactory, have been suggested for this phenomenon. The author regards it as follows: The capacity of a toxin to adsorb an antitoxin does not coincide with its chemical equivalent. On the assumption that m molecules of toxin adsorb $(n+p)$ mols. of antitoxin, that is, more than the number chemically equivalent to it, the result will be a salt-like compound containing an excess of adsorbed antitoxin: $mT+(n+p)A=(T_mA_n+pA)$. If this process proceeds to an end, the system will contain a neutral compound, (T_mA_n+pA), and free toxin, qT, and such a system will undoubtedly be poisonous, in spite of the fact that pA is sufficient to neutralise qT. T. H. P.

Toxins and Antitoxins. IV. New Reaction for Characterising Toxins. I. I. Ostromisslenski (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 313—317. Compare preceding abstracts).—In order to ascertain if there exists an antitoxin corresponding with a given toxin, or if a particular poison represents a toxin, the following method may be employed. In a mixture of 3 c.c. of the toxin or poison with about 3 c.c. of normal serum, 0·36 gram of pure sodium chloride is dissolved, the liquid being maintained at 37—37·5° for three to thirty-six hours. In these conditions the globulin of the serum will, as has been demonstrated, undergo transformation into the corresponding antitoxin. Consequently, if the antitoxin sought really exists, the mixture should become atoxic after this treatment. The solution obtained is introduced into the aural vein of the rabbit or porpoise (A) in quantity considerably exceeding the lethal dose. With a second animal (B) a control experiment is made with a similar amount of the toxin treated in the same way, but without the normal serum. If animal B succumbs whilst A remains living and healthy, it may be asserted that the antitoxin

corresponding with the given toxin does exist, and that it may be applied to the immunisation of animals. If, however, *A* dies, the toxin has no corresponding antitoxin.

With the toxins of tetanus, diphtheria, and botulismus, positive results were obtained, but against morphine and strychnine, normal serum and sodium chloride furnish no protection to animals, and do not even delay their death. T. H. P.

Chemistry of Vegetable Physiology and Agriculture.

Action of Combinations of Poisons on Bacteria. WALTER FREI and ANTON KRUPSKI (*Intern. Zeitsch. phys.-chem. Biol.*, 1915, **2**, 118—196).—The authors have compared the action of various mixtures of substances on bacteria with the actions of their components. The effect produced by a mixture of toxic substances is not a summation of the effects produced by the components, owing to the modifying influence of a physical or chemical nature exerted by the components on each other or on the medium. The toxicity of a substance may be increased, decreased, or unaltered by the addition of a substance which itself does not possess any bactericidal power. The addition of potassium oleate, for instance, which even in 4% aqueous solution is without action on bacteria, to formaldehyde solutions increases their toxicity. Increased toxicity is explained by the assumption of an increased permeability of the cell-walls of the bacteria and a lowered toxicity by a corresponding diminished permeability, but it is pointed out that it may also be due to a change in the solubility of the toxic substance, with a consequent change in its distribution between cell and medium, or to a change in viscosity or surface tension induced by the added substance.

Many substances, such as *m*- and *p*-cresols, β-naphthol, soaps, formaldehyde, glycerol, alcohol, and chloroform, have been examined, alone and in combination, with regard to their toxicity for bacteria, but the results do not at present permit of the enunciation of general laws. H. W. B.

Reducing Properties of Acetic Bacteria. N. L. SÖHNGEN (*Chem. Zentr.*, 1915, **i**, 326; from *Folia mikrobiol. Holländ Beitr. gesamt. Mikrobiol.*, 1914, **3**).—The oxidation of ethyl alcohol to acetic acid, which is characteristic of acetic bacteria, can occur to a slight extent in the reverse sense. The reduction of organic compounds by acetic bacteria, which is chiefly concerned with the formation of ethyl alcohol and of substances which reduce Fehling's solution, was performed under ærobic conditions at 28—30° in an Erlenmeyer flask with a layer of culture liquid about 2 cm. deep. The

latter consisted of a solution of the organic substances in yeast extract. When methylene-blue is added to a flourishing acetic bacteria culture, it is reduced to the leuco-base. In the anærobic region beneath the surface, the following reduction processes have been observed: dextrose is oxidised to gluconic acid, but, simultaneously, ethyl alcohol and acetic acid are formed; aldehydes and ketones could not be detected in the liquid. In anærobic conditions dextrose is decomposed to a slight extent into ethyl alcohol and carbon dioxide. Organic acids and salts are not decomposed by *Acetobakter xylinum* in anærobic conditions. Gluconic acid and calcium gluconate in yeast extract are converted by acetic bacteria into dihydroxyacetone, carbon dioxide, water, and ethyl alcohol (up to 0·4%). Similar experiments with lactic, malic, pyruvic, and acetic acids or their calcium salts show that ethyl alcohol is produced from them in small quantity by the acetic bacteria.

H. W.

The Tyrosine Reagent as a means of Determining the Degree of Decomposition of Albuminoids by Bacteria. Alice Breslauer (*Chem. Zentr.*, 1915, i, 559; from *Zeitsch. Gärungsphysiol.*, **4**, 353—368).—A specimen of tyrosinase from potato peel is purified by repeated precipitation with alcohol; with *p*-cresol alone it gives a characteristic, yellow coloration; with *p*-cresol and most amino-acids a red coloration, which becomes more or less rapidly blue in presence of an excess of the latter. With the help of this reagent, notable differences in the rate of decomposition of different albuminoids are observed in the presence of *Bacillus mesentericus panis viscosi* (Vogel), *B. violaceus Lutiensis* (Macé), *B. subtilis Ehr.* (F. Kohn), *Bacterium prodigiosum* (Ehrenberg), and *Bacillus ruber* (Zimmermann). Further, the influence of different factors on peptolysis could be established in the case of *B. violaceus*. Differences in the coloration with different culture media were only noticed in the presence of gelatin, so that the action of a specific gelatinase might be suspected. In the presence of sugar, gelatin is only attacked in proportion as the sugar is destroyed. The influence of light is not marked, whilst at low temperature the development of the colour is greatly delayed.

Even in very dilute solutions of indole (to 0·0037%) the reagent yields a dye which is soluble in ether, and can be identified, whilst it is indifferent to scatole. The formation of indole by *B. violaceus* and *B. pyocyaneus*, but not by *B. subtilis* or *Staphylococcus pyogenes aureus*, could thus be established. H. W.

Organic Matter in Soil as a Culture Medium for Azotobacter. Florence Annie Mockeridge (*Biochem. J.*, 1915, **9**, 272—283).—A wide range of organic substances is available as a source of energy for this nitrogen-fixing organism in the soil, and any ordinary fertile soil contains abundant food material for its growth. All classes of compounds do not give equally good results, but as a rule the longer the time taken to use the nutrient, the less is the amount of nitrogen fixed. Comparisons are, however, difficult, as

experimental conditions did not allow of the use of the same strain of this ærobic organism throughout. Carbohydrates give the greatest yield of nitrogen fixed; their complex molecule is broken down, and so more energy is liberated. Calculations of the energy available on combustion are given. Starch, dextrin, and gum arabic are approximately equal in this respect, and the ratios of nitrogen fixed to heat of combustion are: 1 : 647, 626, and 676 respectively; the ratio for inulin is 1 : 424; inulin on hydrolysis yields lævulose, and the ratio of lævulose is 1 : 372. Taking starch (1 : 647) and assuming hydrolysis to occur, the figures for dextrin, maltose, and dextrose (1 : 626, 598, and 585) point to an increasing value of the successive products. Experiments are also recorded for aliphatic acids, alcohols, and other organic substances, and the mechanism of fixation discussed. The whole of the available energy is not used in nitrogen fixation, but synthesis of non-nitrogenous material (such as fat) occurs. W. D. H.

Effect of Compounds of Manganese containing Oxygen on Nitrification. G. Leoncini (*Chem. Zentr.*, 1915, i, 1081; from *Staz. sperim. agrar. ital.*, **47**, 777—801).—Numerous experiments showed that the addition of small quantities of manganese dioxide to the soil caused a certain increase in nitrification, but, on the other hand, a distinct decrease in growth was noticeable, which often rendered the advantages of the increased nitrification illusory. In any case, the so-called catalytic manures cannot be accredited with any particular value. G. F. M.

Protein Synthesis in Yeast. W. Zaleski and W. Israilsky (*Ber. Deut. bot. Ges.*, 1914, **32**, 472—479).—Evidence was obtained in support of the view that yeast does not produce proteins directly from ammonia or from single amino-acids, but from a definite mixture of these substances.

As regards single substances, ammonium salts are better as sources of nitrogen for yeast than single amino-acids, as these have first to be broken down to ammonia, from which a suitable mixture of compounds is produced. Asparagine is decomposed by yeast into ammonia and aspartic acid, which is subsequently de-amidated; the results obtained with asparagine are similar to those obtained with a mixture of aspartic acid and ammonium sulphate.

N. H. J. M.

The Co-enzyme of Yeast. Sidney Hagman (*Biochem. Zeitsch.*, 1915, **69**, 403—415).—The difference between the procentual diminution of the rotation and the amount of carbon dioxide evolved in a fermentation with washed yeast and a co-enzyme preparation is negative. The magnitude of this difference depends on the time, the amount of yeast, and phosphate present. A co-enzyme preparation which is free from inorganic phosphates is incapable of activating washed yeast. S. B. S.

Does Peroxydase Exist in Brewers' Yeast? A. Bach (*Arch. Sci. phys. nat.*, 1915, [iv], **39**, 497—507).—Harden and Zilva (A., 1914, i, 1035) have recorded that fresh English yeast gives the

peroxydase colour reaction with hydrogen peroxide and *p*-phenylenediamine. This observation is now disputed, since, on the one hand, very variable results were obtained in experiments with boiled yeast, whilst, on the other hand, in no single instance could a peroxydase reaction be produced, using guaiacol, pyrogallol, or quinol as indicator. The production of the violet coloration in the experiment of Harden and Zilva is attributed to the presence of acids; the intensity of the coloration increases proportionately to the acidity up to the limit 1% acid : 2 of phenylenediamine. The formation of colour in an acidified mixture of *p*-phenylenediamine and hydrogen peroxide is accelerated by finely divided hair in the same manner as by yeast. No peroxydase reaction was obtained with pure races of both top and bottom fermentation yeasts, even when they had been grown in a current of air. Yeast extracts, purified by ultrafiltration, contain invertase and maltase, but no peroxydase. E. F. A.

Paralysis of Enzymes. II. L. Lichtwitz (*Zeitsch. physiol. Chem.*, 1915, **94**, 73—78. Compare A., 1912, ii, 590).—Fermentation by yeast takes place more slowly in a solution containing both sucrose and invert sugar than in pure solutions of either sucrose or invert sugar. This is ascribed to the inhibitory action of invert sugar on the dissociation of the sucrose + invertase complex, and the delayed inversion results in a slower fermentation. At the same time, the invertase of the yeast cells becomes weakened, and sucrose solutions inoculated with yeast cells which have been previously growing in a mixture of sucrose and invert sugar are neither inverted nor fermented so quickly as solutions of sucrose inoculated with the same number of yeast cells grown previously in pure solutions of sucrose or invert sugar. H. W. B.

The Nutrition Balances of the Crude Materials and the Products of Alcoholic Fermentation. Wilhelm Völtz (*Biochem. Zeitsch.*, 1915, **69**, 334—352).—The author, in a communication, which is chiefly of technological interest, calculates, from various data available in the literature, the relative physiological food values of the crude materials, and the finished products and by-products of the beer breweries, and potato-spirit distilleries. S. B. S.

Selection of Nitrogen Compounds by Aspergillus. W. Zaleski and D. Pjukow (*Ber. Deut. bot. Ges.*, 1914, **32**, 479—483).—In solutions containing, in addition to dextrose and minerals, ammonium sulphate and an amino-acid, more ammonia nitrogen is utilised by *Aspergillus* than amino-acid nitrogen; histidine is not taken up at all. With ammonium sulphate and a mixture of amino-acids, *Aspergillus* assimilated more amino-acid nitrogen than ammonia nitrogen.

When, in the place of dextrose, other carbon compounds such as mannitol or glycerol are employed, more nitrogen is assimilated in the form of alanine than in the form of an ammonium salt; and when, in addition to dextrose, ammonium acetate and glycine are

employed, the latter is not utilised at all, although it is utilised in presence of ammonium sulphate and dextrose.

Although the relative amounts of ammonium salts and amino-acids which are assimilated vary according to the conditions, the results show that in presence of a suitable substance as source of carbon, ammonium salts are more readily assimilated by moulds than single amino-acids. Presumably a suitable mixture of amino-acids is better than an ammonium salt. N. H. J. M.

Biochemical and Toxicological Studies on Penicillium puberulum and Penicillium stoloniferum. Decomposition of Maize. CARL L. ALSBERG and OTIS F. BLACK (*Chem. Zentr.*, 1914, ii, 1169—1170. Compare A., 1913, i, 1027).—*Penicillium puberulum* and *stoloniferum*, the chief agents in causing deterioration of maize, are fully described. Pure cultures of the former have a pronounced acid reaction after a prolonged period of culture; the acid, $C_8H_{10}O_4,2H_2O$, m. p. 64—65° (hydrated), 86—87° (decomp. anhydrous), to which the name *penicilliumic acid* is given, can be extracted with chloroform, and separates from water in monoclinic or triclinic, rhombic crystals, which are optically inactive. It is strongly acid to litmus or phenolphthalein, and decomposes carbonates in the cold. It absorbs bromine, yielding insoluble products, and reduces boiling Fehling's solution or cold ammoniacal silver solution. It is very stable towards mineral acids, but sensitive to alkalis. Alkali hydroxides colour the solution yellow, ammonia deep red. The *magnesium* salt forms transparent plates, which contain 30% H_2O and rapidly effloresce; the *alkali*, *alkaline earth*, and *copper* salts are freely soluble, the *lead* salt insoluble, in water; the *silver* salt is unstable. When the acid is boiled with barium hydroxide, barium carbonate is precipitated, and the acidified solution yields a small quantity of crystals with a pleasant odour. When heated with concentrated hydrochloric acid, it gives a yellow oil, which yields a deep red coloration with ferric chloride. Liebermann's reaction gives a carmine-red coloration; a benzoyl derivative could not be prepared by the Schotten-Baumann method. Phenylhydrazine yields a *substance*, lemon-yellow prisms, m. p. 171° (decomp.). Toxicological and physiological investigations show the acid to have strongly marked paralysing action similar to that of phenols and phenolic acids; it tends to inhibit fermentation.

Mycophenolic acid gives a violet colour in aqueous, a bright green colour in alcoholic solution with ferric chloride. It is stable towards acids and alkalis. The *alkali* and *alkaline earth* salts are soluble in water or dilute alcohol; the *copper*, *silver*, and *lead* salts are amorphous and insoluble in water. The acid does not decompose carbonates in the cold; it is without physiological action. H. W.

Metabolism in the Respiration of Sea-algæ. E. PANTANELLI (*Ber. Deut. bot. Ges.*, 1914, **32**, 547—558).—In respiration experiments with *Cystosira abrotanifolia* and *Sargassum linifolium* it was found that the sugar increased, whilst in the case of *Cystosira amentacea* and *Taonia atomaria* there was a loss of sugar.

In closed vessels the amount of insoluble hexosans generally diminishes considerably during respiration; in some cases there was an increase when chloroform was present.

The total nitrogen remained constant in some cases, whilst there was usually a loss, which was sometimes increased and sometimes diminished in presence of chloroform. In some cases there was an increase in protein nitrogen, especially when chloroform was added. N. H. J. M.

A Species of Leguminous Papilionaceæ, newly found to Exhibit Cyanogenesis (Ornithopus L.). M. Gard (*Compt. rend.*, 1915, **161**, 10—11).—The author has examined four different kinds of *Ornithopus*, and in each case has shown the presence of a cyanogenetic compound in the aerial organs of the plant in flower. This compound is decomposed by an enzyme present in the plant, which does not decompose amygdalin. W. G.

Variation in the Composition of the Oil from Species of one and the same Family. G. Pigulevski (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 393—405).—Examination of the oils derived from a number of different genera of each of the families, *Rosaceae*, *Papaveraceae*, *Ericaceae*, *Gramineae*, and *Pinaceae* leads to the following conclusions.

The capacity of plants to produce oil of a definite composition depends on conditions of climate, and possibly also of nutrition. A cold climate induces in plants the necessity of accumulating in the seeds oil exhibiting a high degree of unsaturation, and possessing, therefore, great chemical activity. With morphological changes plants regulate their physiological apparatus for better adaptation to the surrounding conditions, this furnishing an explanation of variations in the composition of the oil in genera of one and the same family. Cultivated genera, occurring in more favourable circumstances than wild ones, lose the power of producing highly unsaturated acids, the iodine number of the oil being consequently higher with the former than with the latter. As regards the acids entering into the composition of the oils, these should show no great differences, and the same acids, namely, oleic, linoleic, and linolenic, probably occur in the oils of genera belonging to different families as well as with those of the same family. T. H. P.

The Nuclein Bases found in the Shoots of Aralia cordata. K. Miyake (*J. Biol. Chem.*, 1915, **21**, 507—509).—These shoots are widely used in Japan as food. Guanine and xanthine were found, but adenine and hypoxanthine not. W. D. H.

Plant Chemistry. P. Q. Keegan (*Chem. News*, 1915, **111**, 289—290).—Analyses of bracken, pink campion, St. John's wort, and water lily. The benzene extract of bracken consisted chiefly of wax, with very little carotin; a subsequent alcohol extract contained catechol tannin and a good deal of sucrose or lævulose. Hot dilute hydrochloric acid extracted a large amount of starch and a

good deal of calcium oxalate. The fronds contained some nitrate. The special chemical feature of the ferns is a large amount of lignin. N. H. J. M.

Some Constituents of the Root of Brauneria angustifolia. FREDERICK W. HEYL and MERRILL C. HART (*J. Amer. Chem. Soc.*, 1915, **37**, 1769—1778).—A proximate analysis of the root of *Brauneria angustifolia* has been recorded by Heyl and Staley (A., 1914, i, 1209). A study has now been made of the constituents of the root, but no physiologically active substance was isolated. The root was extracted with alcohol; the extract after being concentrated under reduced pressure was poured into water, and a brownish-yellow, amorphous, resinous precipitate was obtained. The aqueous liquid yielded small quantities of an *acid*, $C_9H_{10}O_5$, m. p. 207°, which is possibly a trihydroxyphenylpropionic acid; an amorphous glucosidic extract, 0·3%; betaine, 0·1%; sucrose, 7·0%; and lævulose, 4·0%. The resinous precipitate furnished oleic, linoleic, cerotic, and palmitic acids; two isomeric *phytosterols*, $C_{27}H_{46}O$, one with m. p. 154·5—156·5° (*acetyl* derivative, m. p. 131·5—132°), and the other with m. p. 136—137° (*acetyl* derivative, m. p. 118—120°); and a *phytosterolin*, $C_{33}H_{56}O_6$, m. p. 280—290° (*acetyl* derivative, m. p. 163—164°). E. G.

Presence of Acetaldehyde and Hydrogen Cyanide in the Latex of Hevea brasiliensis. M. KERBOSCH (*Rec. trav. chim.*, 1915, **34**, 235—238).—The author has proved the presence of acetaldehyde and hydrogen cyanide in the distillate from the distillation with steam of the latex of *Hevea brasiliensis*, or the serum from the latex previously coagulated by acetic acid. The acetaldehyde was isolated as its *p*-nitrophenylhydrazone, and by this means it was estimated that 1 litre of the fresh latex contained 6 mg. of the aldehyde. W. G.

The Sugars found in the Tubers of Sweet Potatoes. K. MIYAKE (*J. Biol. Chem.*, 1915, **21**, 503—506).—Dextrose, lævulose and sucrose are present, pentose, galactose, mannose, and maltose absent. W. D. H.

Composition of Raphides of Scilla Maritima. HERM. ZIEGENSPECK (*Ber. Deut. bot. Ges.*, 1914, **32**, 630—633).—Calcium oxalate was found in the raphides of *Urginea maritima*. Citric acid was not detected. N. H. J. M.

Alkaloid Formation in Plants. I. The Protein and Nicotine Content of the Tobacco Plant during Growth. H. BAGGESGAARD RASMUSSEN (*Biochem. Zeitsch.*, 1915, **69**, 461—466).—The content of total nitrogen alters during the growth of the plant, diminishing with the age. The lower leaves contain less nitrogen than the higher ones. The nitrogen is higher in well-fertilised plants. In the less fertilised plants the protein nitrogen diminishes with the age. The nicotine content (estimated by a method not yet

published and precipitated by silicotungstic acid) increased during the whole period of the growth. The basic nitrogen also increases. There are large variations in the proportions of nicotine to basic nitrogen. S. B. S.

The Carboxylases of Plants. W. ZALESKI (*Ber. Deut. bot. Ges.*, 1914, **32**, 457—458).—Ground pea and yellow lupin seeds, and the ends of stalks of etiolated *Vicia Faba* plants, which decompose pyruvic acid into carbon dioxide and acetaldehyde (*ibid.*, **31**, 349), also decompose oxalacetoacetic acid, first into pyruvic acid and then into carbon dioxide and acetaldehyde.

Other ketonic acids (phenylpyruvic acid, chelidoneacetonedicarboxylic acid, and lævulic acid) gave negative results.

N. H. J. M.

Nitrogen Distribution in Feed-stuffs and Cereals. J. F. BREWSTER and C. L. ALSBERG (*Proc. Soc expt. Biol. Med., New York*, 1915, **12**, 192—193).—The finely ground material (maize, cotton-seed flour, Kaffir corn, etc.) was, after hydrolysis with 20% hydrochloric acid, subjected to Van Slyke's method. The estimation of sulphur proved a difficulty; the values for cystine were low, and no doubt sulphur is also present in other combinations. Kaffir corn and tomato seed meal lack histidine; tryptophan is present in the latter, but only in traces in the former. Lysine and tryptophan are present both in maize and cotton-seed. W. D. H.

The Protein Substances of Barley, in the Grain Itself and During the Brewing Process. H. SCHJERNING (*Compt. rend. Lab. Carlsberg*, 1914, **11**, 45—105 Compare A. 1907, ii. 46).—A summary of the results published in 1906, 1910, and 1913, with a description of the methods employed in estimating the different groups of proteins. N. H. J. M.

Melanoidins and their Occurrence in Kiln Malt. WILLY RUCKDESCHEL (*Chem. Zentr.*, 1914, ii. 1114—1115).—Maillard's reaction (according to which amino-acids give brown and aromatic products with dextrose and other sugars) has been applied to the amino-acids and other substances containing nitrogen which are found in malt. According to the author, the following amino-acids yield coloured compounds: glycine, the taste of the product is acidic, N content 5·28%; alanine, N content 5·05%; phenylalanine, odour of faded roses, taste bitter; leucine, odour of bread, and hence an important component in the formation of the aroma of malt; valine reacts slowly. The following amines of malt give coloured products: ammonia, methylamine, trimethylamine, choline, and asparagine; tyrosine, allantoin, and betaine do not give Maillard's reaction.

In the formation of melanoidins the amino-group of the amino-acid reacts with the aldehyde groups of two molecules of dextrose with the formation of water; simultaneously carbon dioxide is eliminated from the carboxyl group of the amino-acid. It is there-

fore a case of the formation of definite chemical products, and not of caramelisation of dextrose; for example, glycine-melanoidin yields a pyrrole when distilled with zinc dust. When dextrose is heated with amino-acids in concentrated aqueous solution, the acidity of the solution diminishes with increase in colour. The velocity of the reaction is generally greatly increased by increase in concentration, temperature, or pressure. An excess of dextrose retards the reaction. Of amino-acids, glycine and alanine react most readily, then the polypeptides, and finally leucine; reaction occurs more rapidly with the amines.

The melanoidins are emulsion colloids, and appear in a soluble (reversible) and an insoluble (non-reversible) form. Precipitation with neutral salts and non-electrolytes yields a product soluble in water, whilst, under the influence of electrolytes or of an electric current the insoluble form is precipitated. Strong heating destroys the coloration and the aroma of the substances. An excess of dextrose checks the transformation of melanoidins into the insoluble form. When the solutions are shaken with air, a relatively stable froth is obtained. Solutions of the synthetic melanoidins are not fermented by yeast cultures.

When an aqueous extract of green malt is evaporated, the rapidity with which the colour deepens and the aroma is developed is similar to that observed during the preparation of synthetic melanoidins. Investigation of the amino-acids and polypeptides in malt at different stages of kilning gives results, with respect to the development of colour and aroma, which agree with those obtained with the synthetic products. Taken in conjunction with the diminution of amino-acid content during kilning, the evidence thus adduced is considered conclusive with regard to the part played by amino-acids and polypeptides in the production of colour and aroma in kiln malt. H. W.

Basal Rot of the Sugar-beet. J. Bodnár (*Biochem. Zeitsch.*, 1915, **69**, 245—256).—This disease appears to be of bacterial origin, and spreads from the tips of the roots upwards. A comparison was made of the chemical composition of normal and healthy roots. The diseased roots contain the larger amount of water and acid, less sucrose, and more invert sugar, and a larger amount of inorganic constituents (ash), especially of aluminium. S. B. S.

Distribution of Invertase in the Tissues of Beet at Different Periods of Vegetation. H. Colin (*Compt. rend.*, 1915, **160**, 777—779).—The leaves of beet rapidly invert sucrose when immersed in solutions of it. The hydrolysing power of the stems diminishes from the leaf end to the base, where it scarcely exists. The root, in normal conditions, has no action on sucrose, and only acquires the power of inverting sucrose when æration is deficient.

The conclusion is drawn that if sucrose is elaborated in the root, this is not brought about by an invertase similar to that which is

readily detected in the stems. Sucrose can only accumulate in the leaves if formed more rapidly than the rate of the hydrolysis.

When stored with precautions, the root shows a very slight increase in reducing sugar, and the presence of sucrase cannot be detected. In the second year, up to the time when the seed ripens, it is the same. The sucrose passing from the root to the stems can only be utilised by the aerial parts after being hydrolysed.

N. H. J. M.

Osmosis in Soils. C. J. Lynde and J. V. Dupré (*Proc. Roy. Soc., Canada*, 1914, [iii], **8**, 133—138).—With a concentrated soil solution, as solution, and a column of soil (about 6·5 cm. deep) as semi-permeable membrane, an osmotic pressure was observed equal to that of a column of water about 3·5 m. high. The results indicate that the pressures are not due to the swelling of the soil, but to osmosis. The soil employed resembles the usual semi-permeable membrane in being probably in a colloidal state, and in absorbing water more readily than it does a soil solution; the movement is towards the soil solution as the liquid least absorbed.

The movement of soil water is, therefore, subject to osmosis, as well as to gravitational, capillary, and thermal movement.

N. H. J. M.

Chemistry of Soils. Evolution of Amino-acids. Gaston Chardet (*Rev. gen. Chim. pure appl.*, 1914, **17**, 137—144).—A general survey of the chemistry of the changes occurring in the nitrogen compounds of the soil, and in particular of the formation of amino-acids and other decomposition products of proteins in the soil. In the latter part of the paper a detailed account is given of a way of applying Sörensen's method, as modified by Bailly (A., 1912, ii, 1009), to the estimation of amino-nitrogen in the soil.

W. G.

Chemistry of Soils. Evolution of Purines. Gaston Chardet (*Rev. gen. Chim. pure appl.*, 1914, **17**, 154—155. Compare preceding abstract).—A brief account of our present knowledge with regard to the degradation of nucleo-proteins and the formation of purine bases in the soil.

W. G.

Chemistry of Soils. Evolution of Carbon. Gaston Chardet (*Rev. gen. Chim. pure appl.*, 1914, **17**, 214—218. Compare two preceding abstracts).—A brief summary of the changes occurring in the degradation of cellulose and its derivatives in the soil, and in particular a discussion as to the mode of formation of humic acids in the soil.

W. G.

Alkaline Reaction of the Soil Caused by Acids in Relationship to the Nourishment of Plants. I. Solubility of Iron Compounds in the Soil. Giulio Masoni (*Chem. Zentr.*, 1915, i, 498; from *Staz. sperim. agrar. Ital.*, 1914, **47**, 674—701).—The author has extended his previous investigations to chalky soils containing compounds of iron. The phenomenon of chlorosis in such soils is attributed to the separation of insoluble iron com-

pounds by the alkaline solutions which are formed in the soil. For details, the original paper must be consulted. H. W.

Lithium in Soils. L. A. STEINKOENIG (*J. Ind. Eng. Chem.*, 1915, **7**, 425—426).—Numerous samples of soils from different parts of the United States were all found to contain lithium, the quantity of lithia present varying from 0·001 to 0·008%. Practically the same amounts were found in the respective soils and sub-soils. W. P. S.

Estimation of the Sulphofying Power of Soils. P. E. BROWN and E. H. KELLOGG (*J. Biol. Chem.*, 1915, **21**, 73—89; *Centr. Bakt. Par.*, 1915, ii, **43**, 552—601).—This is estimated by adding sodium sulphide or, better, sulphur to fresh soil, adjusting the amount of moisture, and concentrating for five to ten days at room temperature. The sulphates are then leached out by shaking with water for seven hours, precipitated by barium chloride, and then estimated by the sulphur photometer.

The oxidation is caused by bacteria. There is some slight chemical oxidation also of sulphides on shaking with water, but no such change occurs with free sulphur. The use of manure on soils increases their sulphofying power. The optimum moisture is 50% of that required for complete saturation; increase of the air content in the soil raises the power. Carbohydrates depress it.
W. D. H.

Analysis of Plants and Soils to Estimate the Amount of Nutritive Substances in Soils. TH. PFEIFFER, E. BLANCK, W. SIMMERMACHER and W. RATHMANN (*Landw. Versuchs-Stat.*, 1915, **86**, 339—391).—The amount of nitrogen taken up by plants from an unmanured soil is only slightly increased by manuring with an excess of phosphoric acid and potassium. Assimilation of phosphoric acid, on the other hand, is much more influenced by applications of nitrogen and potassium, partly owing to greater root development and partly to increased solubility of the soil phosphates, which will vary with different soils. The same holds good in the case of potassium.

Oat plants assimilated only about 10% of the phosphoric acid dissolved by 1% hydrochloric acid, whilst with potassium the results were in much greater agreement. Water saturated with carbon dioxide dissolved much less phosphoric acid than was assimilated by oats in the same soil. In this case, the difference is attributed to the presence of organic acids in the roots, to the dissolving action of manurial salts, and to disturbances in the equilibrium of the soil solution.

The potassium fixed by absorption in soils, as estimated by Kellner, cannot be the only source of potassium available to plants.

Whilst it is found that neither analysis of plants nor soil analysis, as employed, are unsuitable for establishing the amounts of nutrients in soils, it is considered likely that useful indications will be obtained by ascertaining the maximum amounts of nutritive

substance which give increased yields, although the results of Liebscher and van Seelhorst show that difficulties exist. Soils which yield crops relatively poor in phosphoric acid, when manured with nitrogen and potassium, sometimes respond only slightly, if at all, to applications of phosphates, whilst a fairly high amount of phosphoric acid in a crop may sometimes be increased by phosphatic manure. N. H. J. M.

Manurial Value of Sodium Chloride. B. SCHULZE (*Landw. Versuchs-Stat.*, 1915, **86**, 323—330).—The results of pot experiments with white mustard in a soil deficient in potassium showed that addition of potassium zeolite (prepared from a calcium zeolite and potassium chloride) caused a very great increase in the yield of the first crop. Subsequent crops were much less, and addition of sodium chloride failed to liberate potassium from the zeolite.

In similar experiments with another soil, addition of potassium zeolite gave a slightly increased yield, whilst the amount of potassium assimilated was nearly doubled, and the amount of sodium assimilated slightly diminished. With sodium chloride, in addition to potassium zeolite, there was a further slight increase in yield, no appreciable difference in the amount of potassium assimilated, and a considerable increase in the amount of sodium assimilated.

The conclusion is drawn that sodium chloride has a direct manurial value in the case of some plants, and that it does not liberate potassium from potassium zeolites. N. H. J. M.

Cyanamide, Dicyanodiamide, and Calcium Cyanamide. J. C. DE RUIJTES DE WILDT and A. D. BERKHOUT (*Bied. Zentr.*, 1915, **44**, 151—155; from *Versl. Landbouwk. Onders. Rykslandbouwproefstat*, 1913, No. 13).—Cyanamide (0·5%), when kept for three years in $N/50$-solutions of sodium, ammonium, and potassium chlorides, was only slightly decomposed; in presence of calcium chloride ($N/50$) and calcium carbonate, decomposition was more marked. Mineral acid solutions ($N/50$) containing 0·5 and 1·0% of cyanamide, which were kept for two months, were found to contain carbamide.

The results of pot experiments in which buckwheat grown in humus sand received cyanamide and iron oxide showed that the iron was without effect.

Decomposition of calcium cyanamide when stored is shown to be due to atmospheric moisture rather than to carbon dioxide; production of dicyanodiamide is to be expected more than loss as ammonia.

Calcium cyanamide may be mixed with potassium sulphate, magnesia, and kainite.

The results of manurial experiments with fresh and with stored calcium cyanamide showed that the value of the stored manure was considerably less than that of the fresh. N. H. J. M.

Organic Chemistry.

Process for Hydrogenation and Dehydrogenation of Carbon Compounds. BADISCHE ANILIN- & SODA-FABRIK (Fr. Pat. 473697; from *J. Soc. Chem. Ind.*, 1915, **34**, 734).—Hydrogenation and dehydrogenation of carbon compounds by means of catalysts other than those of the platinum-palladium group can be carried out more readily and at lower temperatures when the catalysts are mixed with (*a*) oxy-compounds of the earth metals, including rare metals, beryllium, and magnesium; (*b*) other oxy-compounds, particularly those of titanium, uranium, manganese, columbium, tantalum, chromium and boron, which are fusible and reducible only with difficulty; (*c*) silica; (*d*) sparingly soluble salts of the alkaline earth metals or lithium with oxy-acids of phosphorus, molybdenum, tungsten, selenium, or with fluorine, tellurium or antimony. The catalysts are prepared by precipitating, melting, or grinding together compounds from which the metallic catalyst is to be obtained with salts of the activating substance, and reducing the product with hydrogen, or a mixture of hydrogen and carbon monoxide. Thus a mixed precipitate of nickel and beryllium carbonates is reduced at 250—300° with carbon monoxide and hydrogen until the nickel oxide is reduced and the carbon monoxide is completely converted into methane. The catalyst may then be cooled to 150° without losing its activity. The presence of a trace of alkali in the activating substance is advantageous.

G. F. M.

The Adsorption of Acetylene by Colloidal Platinum, Iridium and Osmuim, and by Platinum Black. C. PAAL and ANTON SCHWARZ (*Ber.*, 1915, **48**, 1195—1202).—It has already been shown (Paal and Hohenegger, A., 1913, i, 241) that palladium in colloidal solution as well as in the form of palladium black, wet or dry, can adsorb large quantities of acetylene, but that the process occurs with a steadily diminishing rate due to the formation of polymerisation or condensation products which envelope the particles of metal. Colloidal platinum solution behaves in a similar manner in adsorbing acetylene, but, again, after once being exposed to acetylene the colloidal solution does not regain its activity on keeping; platinum black also adsorbs acetylene, but to a much less extent than palladium black.

[With F. BIEHLER and CHR. GOES.]—Colloidal solutions of iridium and osmium are indifferent to acetylene. D. F. T.

Catalytic Actions of Colloidal Metals of the Platinum Group. XIV. The Graded Hydrogenation of Acetylene with Colloidal Platinum. C. PAAL and ANTON SCHWARZ (*Ber.*, 1915, **48**, 1202—1207).—As has already been demonstrated (Paal and Hohenegger, this vol., i, 113), acetylene can be reduced by hydrogen and colloidal palladium solution, so that a 70% yield of ethylene is

obtained, but a disadvantage lies in the considerable adsorption of acetylene by the colloidal metal (Paal and Hohenegger, A., 1910, i, 806, 807; 1913, i, 241), so that some of this gas is prevented from hydrogenation. Attempts to replace the palladium by platinum now show that the reduction is effected much more slowly by this metal, and that the yield of ethylene is lower on account of a greater proportion of the gas undergoing reduction to ethane. D. F. T.

Preparation of Dichlorodinitromethane by the Simultaneous Nitration and Chlorination of Acetone. J. N. Rakshit (T., 1915, **107**, 1115—1117).—Dichlorodinitromethane was obtained as a heavy pale yellow oil by the action of concentrated nitric acid on acetone in presence of a large quantity of granulated calcium chloride. The reaction commenced with considerable violence in twenty to twenty-five minutes, and nitrous fumes, chlorine, and nitrosyl chloride were evolved. After the calcium chloride had dissolved, the upper nitric acid layer was separated and again treated as before, the whole experiment lasting six hours. More than 40 c.c. of acetone should not be treated at once on account of the danger of explosion. The yield of the pure product, b. p. 121—122·5°, was much better than that obtainable by other methods. G. F. M.

Formation of Alcohol from Wood. Erik Hägglund (*J. pr. Chem.*, 1915, [ii], **91**, 358—364).—The author has investigated the hydrolysis of wood (pine and fir sawdust) by dilute hydrochloric acid, aqueous sulphur dioxide, calcium hydrogen sulphite, and concentrated hydrochloric and sulphuric acids, under varying conditions of temperature, at different concentrations, and with varying amounts of acid, determining not only the percentage of sugar produced but also the yield of alcohol derived therefrom by fermentation. The best results were obtained by carrying out the hydrolysis with 70% sulphuric acid for forty-eight hours at 18°, using wood and acid in equal proportions by weight; the percentage of sugar amounted to 54·8, calculated on the weight of dry wood, the yield of alcohol to 158 litres per ton.

In all cases, however, either the cost of the initial material and acid is too great, or the yield of alcohol too small, for the process to be of commercial value. F. B.

Some Symmetrical Bitertiary Glycols. M. Bouvet (*Bull. Soc. chim.*, 1915, [iv], **27**, 202—216).—The author has prepared a number of symmetrical bitertiary glycols by the action of an excess of different organo-magnesium compounds on ethyl adipate.

In this way magnesium methyl iodide and ethyl adipate yielded $\beta\eta$-dimethyloctane-$\beta\eta$-diol (compare Zelinski and Kravetz, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 931), which gives a *hydrate*, $C_{10}H_{22}O_2,2H_2O$, m. p. 59°. By the action of gaseous hydrogen chloride or an excess of concentrated hydrochloric acid on a cold solution of this glycol in toluene or alcohol, *$\beta\eta$-dichloro-$\beta\eta$-dimethyloctane*,

$$CMe_2Cl\cdot[CH_2]_4\cdot CMe_2Cl,$$

m. p. 49°, was obtained, which on heating with pyridine in alcoholic solution for ten hours yielded *βη-dimethyl-Δ$^{\beta\zeta}$-octadiene*,

$$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2,$$

b. p. 163·5—164·5°.

By the action of magnesium ethyl iodide on ethyl adipate, *γθ-diethyldecane-γθ-diol*, $OH{\cdot}CEt_2{\cdot}[CH_2]_4{\cdot}CEt_2{\cdot}OH$, m. p. 72—73°, was obtained. Similarly, magnesium propyl iodide yielded *δι-dipropyldodecane-δι-diol*, $OH{\cdot}CPr_2{\cdot}[CH_2]_4{\cdot}CPr_2{\cdot}OH$, m. p. 93°. The magnesium derivative of bromobenzene reacted with ethyl adipate in ethereal solution to give *aaζζ-tetraphenylhexane-aζ-diol*, $OH{\cdot}CPh_2{\cdot}[CH_2]_4{\cdot}CPh_2{\cdot}OH$, m. p. 211·5°, together with some diphenyl. This glycol was insoluble in water, but soluble in most organic solvents. It gave no coloration with concentrated hydrochloric acid, but with concentrated sulphuric acid in the cold gave an orange-red coloration, the parts exposed to the air turning pale blue. From the products of this action a *substance* was isolated, m. p. 148°. When the glycol was heated either with glacial acetic acid or a mixture of this acid with concentrated hydrochloric acid it was dehydrated, yielding *aaζζ-tetraphenyl-Δ$^{a\epsilon}$-hexadiene*,

$$CPh_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CPh_2,$$

m. p. 108°, which in chloroform solution took up four atoms of bromine, giving a *tetrabromide*, m. p. 140° (decomp.). Tetraphenylhexadiene in amyl alcohol on the addition of sodium, followed by boiling of the solution, was converted into *aaζζ-tetraphenylhexane*,

$$CHPh_2{\cdot}[CH_2]_4{\cdot}CHPh_2,$$

m. p. 104°. On oxidation with potassium permanganate or chromic acid in acetone solution, tetraphenylhexadiene yielded benzophenone and succinic acid, this reaction being the last stage in a passage from adipic to succinic acid.

By the action of ethyl adipate on magnesium benzyl chloride, *aaζζ-tetrabenzylhexane-aζ-diol*, needles, m. p. 181·5—182°, was obtained, together with a considerable quantity of dibenzyl. The glycol gave a yellow coloration with concentrated sulphuric acid, but showed no sign of decomposition.

Attempts to prepare a *cyclo*hexylhexanediol were not very successful. The interaction of ethyl adipate and magnesium *cyclo*hexyl chloride gave a very small yield of *aaζζ-tetracyclohexylhexane-aζ-diol*,

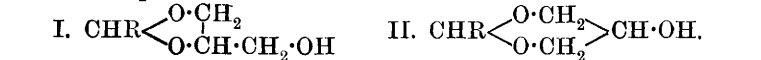
$$OH{\cdot}C(C_6H_{11})_2{\cdot}[CH_2]_4{\cdot}C(C_6H_{11})_2{\cdot}OH,$$

m. p. 158°, the main products being various dehydration products of this glycol, which could not be separated and isolated in the pure state, some *cyclo*hexene and some *cyclo*hexyl ethyl ether, b. p. 149°.

W. G.

Structure of Methyleneglycerol and Cinnamylideneglycerol. (Preliminary Note.) David Henry Peacock (T., 1915, **107**, 815—818. Compare Irvine, Macdonald and Soutar, T., 1915, **107**, 337).—The author has obtained evidence of the resolution of the *hydrogen phthalate* of methyleneglycerol into optically active forms by the crystallisation of its *brucine* salt, and therefore decides in favour of the first of the two following formulæ (R = H) for methyleneglycerol,

the second formula being excluded as it does not admit of the existence of enantiomorphous isomerides.



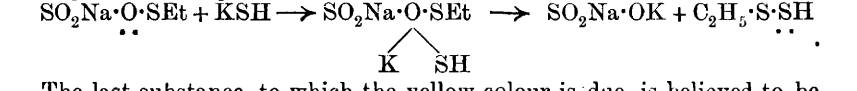
The o-*nitrobenzoate* of methyleneglycerol has m. p. 135°; the *phenylurethane*, $NHPh\cdot CO_2\cdot C_4H_7O_2$, m. p. 129°.

Cinnamylideneglycerol (I. or II., R = CHPh:CH·) forms a viscid oil, solidifying to a crystalline mass, m. p. 110—112°. When heated with phenylcarbimide until a vigorous reaction occurs, it yields a *phenylurethane*, m. p. 107°; if the components are heated for one hour at 150°, an isomeric *phenylurethane*, m. p. 170°, is produced. The isomerism is probably steric, being determined either by the relative positions of the styryl and phenylcarbamyl groups with respect to the plane of the heterocyclic ring, or by the spatial arrangement of the groups attached to the double linking of the styryl group. The author hopes that an examination of the reduction products and additive compounds with hydrogen bromide will throw further light on this point. F. B.

Process for Eliminating the Elements of Water from Organic Hydroxy-compounds. J. D. Riedel A.-G. (D.R.-P. 281902; from *J. Soc. Chem. Ind.*, 1915, **34**, 735).—When organic hydroxy-compounds are heated with glycollic acid or glycollide, water is eliminated to the almost complete exclusion of secondary reactions. The reaction may be carried out under diminished pressure, and no excessive frothing occurs. Acraldehyde is thus, for example, obtained from glycerol and glycollic acid, pyruvic acid from tartaric acid and glycollic acid, and dipentene from terpineol and glycollide. G. F. M.

Action of Alkali Sulphide on Sodium Ethyl Thiosulphate. A. Gutmann (*Ber.*, 1915, **48**, 1162—1166).—An extension of the investigation of the behaviour of sodium ethyl thiosulphate towards alcoholic sodium hydroxide (Gutmann, A., 1907, i, 671; 1908, i, 497).

In warm alcoholic solution, sodium ethyl thiosulphate reacts with potassium sulphide, giving a deep yellow solution and a deposit of potassium sulphite. The solution when boiled becomes colourless and sulphur separates; a solution of potassium cyanide or sodium arsenite also decolorises the yellow solution. It is suggested that the action of potassium sulphide follows the course:



The last substance, to which the yellow colour is due, is believed to be present in the solution as *thioethyl potassium persulphide*, $C_2H_5\cdot S\cdot SK$, which readily decomposes into ethyl mercaptan and sulphur. The additional valencies in the above formulæ are in accord with the author's views as to the cause of the reactivity of the atoms affected.

D. F. T.

Preparation of Chloroformic Acid Esters. A. Hochstetter (D.R.-P. 282134; from *J. Soc. Chem. Ind.*, 1915, **34**, 686).—Chloro-

formic acid esters are obtained in good yields by the action of carbonyl chloride, dissolved in a solvent immiscible with water, on an alcohol or phenol distributed between this solvent and a layer of water. Inert salts are dissolved in the water if necessary in order that a considerable portion of the alcohol may be present in the layer containing the carbonyl chloride. The non-aqueous layer may be composed of the chloroformic ester which is being prepared or of liquefied carbonyl chloride. G. F. M.

Preparation of Amyl Acetate. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 282266; from *J. Soc. Chem. Ind.*, 1915, **34**, 686).—The action of aluminium amyloxide on acetaldehyde in amyl alcohol solution results in the formation of amyl acetate and ethyl alcohol, and the products can be separated by fractional distillation. G. F. M.

Heneicosoic Acid. HENRY RONDEL LE SUEUR and JOHN CHARLES WITHERS (T., 1915, **107**, 736—739).—Of the normal acids of the acetic series up to and including the acid containing twenty-two carbon atoms, only *heneicosoic acid*, $C_{20}H_{41}\cdot CO_2H$, has hitherto not been described. The missing acid has now been prepared in almost quantitative yield by the reduction of μ-ketoheneicosoic acid (T., 1914, **105**, 2800) with amalgamated zinc and hydrochloric acid according to Clemmensen's method (A., 1913, i, 733). It crystallises in stellar aggregates of stout needles, m. p. 73—74°, and forms a white *silver* salt and *methyl* ester, thin, lustrous scales, m. p. 49°; the *chloride* reacts with ammonia, yielding the *amide*, aggregates of needles, m. p. 110°, and with bromine to form a bromo-acid chloride, which is converted by successive treatment with water and boiling aqueous potassium hydroxide into *α-bromoheneicosoic acid*, slender needles, m. p. 65·5—66·5°, and *α-hydroxyheneicosoic* acid, aggregates of needles, m. p 93—94°, respectively.

It is also mentioned that θ-ketomargaric acid is readily reduced by Clemmensen's method to margaric acid. F. B.

Organic Per-Acids. J. D'ANS and A. KNEIP (*Ber.*, 1915, **48** 1136—1146).—In an earlier investigation (D'Ans and Frey, A., 1912, i, 601) the preparation of several organic per-acids has been described, but performic acid was obtained only as a solution of approximately 50% concentration. By applying the same method but with an increased proportion of sulphuric acid (compare D'Ans and Frey, A., 1914, i, 10) in the reaction mixture, a 90% solution has now been obtained; this was a clear liquid which was unstable and gradually decomposed into water and carbon dioxide, a concurrent hydrolysis into formic acid and hydrogen peroxide also occurring but to a smaller extent. The instability of performic acid is indicated by a heat of decomposition into carbon dioxide and water estimated at 92 Cals. per gram molecule, and certain substances such as zinc dust, lead oxide, and sodium azoimide induce explosive decomposition of the 90% solution.

Modifications of the original method for preparing peracetic acid are described and a warning is issued on account of the variable reactivity of acetic anhydride with pure hydrogen peroxide; traces of sulphuric

acid greatly activate the acetic anhydride. Peracetic acid is much more stable than performic acid, and no appreciable decomposition occurs in a 50% solution during a fortnight; solutions of this substance therefore promise to be of considerable use for oxidising purposes in place of Caro's acid, an additional advantage existing in the possibility of varying the solvent. It is shown that with a solution of peracetic acid, aldehydes are oxidised to acids, primary aromatic amines to nitroso-, azoxy-, and azo-compounds, whilst azo-compounds are converted into azoxy-compounds. D. F. T.

Catalytic Reduction of Unsaturated Fats and Fatty Acids by Nickel Oxides. E. ERDMANN (*J. pr. Chem.*, 1915, [ii], **91**, 469—506).—This paper contains an historical review of the literature dealing with the reduction of unsaturated fats and fatty acids, together with a reply to Meigen and Bartels' criticism (A., 1914, i, 482) of Bedford and Erdmann's work (A., 1913, i, 70) on the catalytic reduction by hydrogen at ordinary pressures in the presence of nickel oxide.

Meigen and Bartels maintain that nickel oxide can only act as a catalyst after it has been previously reduced to metallic nickel, their view being based on (1) the detection of the free metal in the catalyst, after the reduction is complete, by means of the nickel carbonyl reaction and also by analysis, and (2) the greater rate of hardening in the presence of metallic nickel as compared with that when nickel oxide is employed.

The author now describes a number of experiments, which prove conclusively that cotton-seed and other unsaturated oils are hardened at a far greater rate by the oxide than by metallic nickel. Further, the analysis, electrical conductivity, and density of the recovered catalyst show that when nickel oxide is used, the formation of metallic nickel can be completely avoided.

In the experiments carried out by Meigen and Bartels with the oxide, the presence of metallic nickel in the recovered catalyst is due to the employment of impure oils containing reducing substances, the application of too high a temperature, the addition of too large an amount of the catalyst, and also to the hardening process being carried too far.

Moreover, a positive nickel carbonyl reaction can only be taken as a sure indication of the presence of metallic nickel when the reaction is carried out at a comparatively low temperature; at 80—90°, the temperature employed by Meigen and Bartels, carbon monoxide exercises a reducing action on nickel oxide with the formation of carbon dioxide and nickel carbonyl.

The author is of the opinion that the true catalyst concerned in the reduction is not the suboxide, Ni_3O, but a hydride of the composition H·Ni·O·Ni·OH or H·Ni·O·NiH, a view which finds support in the peculiar behaviour of nickel hydroxide when heated in an atmosphere of hydrogen (Berger, A., 1914, ii, 656), and also in the liberation of both hydrogen and water when the recovered catalyst, after drying at 100°, is heated under diminished pressure or in a current of inert gas at 250°. F. B.

Metal Content of Some Linoleates and "Rosinates." L. G. RADCLIFFE and C. W. PALMER (*J. Soc. Chem. Ind.*, 1915, **34**, 644—645).—A number of pure and commercial "rosinates" have been examined for their metal and water content. The pure salts of cobalt, lead and manganese were prepared by precipitation from a solution of potassium abietate obtained from crystalline abietic acid. The metal content in each case was in agreement with the formula $(C_{19}H_{29}\cdot CO_2)_2M''$. A description of the preparation and uses of the commercial rosinates and linoleates is given, together with their metal content and loss on drying at 100—104°. G. F. M.

Mixed Glycerides of Linseed Oil. G. SCHICHT (*Chem. Zentr.*, 1914, ii, 411; from *Seifenfabrikant.*, 1914, **34**, 673—674).—Linseed oil contains mixed triglycerides of stearic, palmitic, and unsaturated acids. La Plata linseed oil was exposed to a temperature of $-8°$ to $-10°$, and the crystalline deposit was separated and allowed to crystallise at $-10°$ from acetone. After repeated crystallisation from light petroleum, alcohol and ether, a white, crystalline substance was obtained, m. p. 33—34°, the constants of which are in accord with the requirements of a *linoleopalmitostearin*,

$$C_3H_5(O\cdot CO\cdot C_{17}H_{31})(O\cdot CO\cdot C_{15}H_{31})(O\cdot CO\cdot C_{17}H_{35}).$$

From the mother liquors, a crystalline mass, m. p. 31—32°, was separated, an examination of the unsaturated fatty acids, and determination of the constants of which indicated that it consisted of mixed glycerides of oleic, linoleic, and stearic acids, probably *dioleostearin* and *linoleodistearin* in the proportions of 1 to 2. A substance which was probably an *oleolinoleopalmitin* was also isolated. The above glycerides amount to scarcely ½% of the weight of the oil, and the remaining 9—10% of saturated fatty acids must therefore be components of glycerides of very low melting point. G. F. M.

Iodosuccinic Acids. A. WESTERLUND (*Ber.*, 1915, **48**, 1179—1183).—Inactive bromosuccinic acid reacts with sodium iodide in acetone solution (compare Finkelstein, A., 1910, i, 453), yielding inactive iodosuccinic acid (compare Holmberg, A., 1913, i, 824; 1914, i, 139). With *l*-bromosuccinic acid the same inactive product was obtained, the lack of optical activity being due to the ready racemisation of active iodosuccinic acids by iodides in aqueous or acetone solution. The racemisation follows the course of an unimolecular reaction. D. F. T.

The Rotation of *iso*Butyl Diacetyl-*d*-tartrate. THOMAS STEWART PATTERSON and DONALD NEIL MCARTHUR (T., 1915, **107**, 814—815).—The rotation of iso*butyl diacetyl*-d-*tartrate*, a liquid, b. p. 183°/11 mm., prepared from *iso*butyl *d*-tartrate and acetyl chloride, has been determined, both in the pure state and in nitrobenzene solution, over a wide temperature interval. The homogeneous ester shows a minimum value of $[M]_D$ 51·57° at 70°, which appears to be displaced by virtue of solution in nitrobenzene, towards a lower temperature and also towards a lower rotation value. F. B.

Syntheses with the Aid of Monochloromethyl Ether. III. Action of Monochloromethyl Ether on the Sodium Derivatives of Ethyl Ethane-$\alpha\beta\beta$-tricarboxylate, Ethyl Butane-$\alpha\alpha\delta\delta$-tetracarboxylate, and Ethyl Pentane-$\alpha\alpha\epsilon\epsilon$-tetracarboxylate. JOHN LIONEL SIMONSEN (T., 1915, **107**, 783—792).—The interaction, in benzene solution, of monochloromethyl ether with the sodium derivatives, mentioned in the title, results in the formation of ethyl γ-methoxypropane-$\alpha\beta\beta$-tricarboxylate, ethyl $a\zeta$-dimethoxyhexane $\beta\beta\epsilon\epsilon$-tetracarboxylate, and ethyl ζ-methoxyhexane-$\alpha\alpha\epsilon\epsilon$-tetracarboxylate respectively. The method, previously employed by the author (T., 1908, **93**, 1781) for the preparation of *cis-cyclo*butane-1 : 3-dicarboxylic acid from ethyl δ-methoxybutane-$\alpha\alpha\gamma\gamma$-tetracarboxylate, does not appear to be of general application for the preparation of cyclic compounds, for ethyl γ-methoxypropane-$\alpha\beta\beta$-tricarboxylate, on hydrolysis with hydrochloric acid, does not yield the expected *cyclo*propane-1 : 2-dicarboxylic acid, but is converted into itaconic acid, which is obtained more readily in this manner than by any method hitherto described.

Ethyl γ-methoxypropane-$\alpha\beta\beta$-tricarboxylate, a mobile oil, b. p. 161°/7 mm., is hydrolysed by alcoholic potassium hydroxide to the free *acid*, decomp. 145—146°, which forms a flocculent *silver* salt, and loses carbon dioxide at 150°, yielding *γ-methoxypropane-$\alpha\beta$-dicarboxylic acid*, nodules of slender needles, m. p. 102°, *silver* salt, microscopic plates. The last-named acid yields citraconic anhydride on distillation under ordinary pressure, and when heated with acetyl chloride is converted into an oily *anhydride* of γ-chloropropane-$\alpha\beta$-dicarboxylic acid. Its constitution has been established by the formation of γ-bromo- and γ-iodopropane-$\alpha\beta$-dicarboxylic acids (compare Swarts, *Jahresber.*, 1866, 722) by the action of hydrobromic and hydriodic acids; of these two dicarboxylic acids, the former is converted by boiling with alcoholic potassium hydroxide into mesaconic acid.

Ethyl $a\zeta$-dimethoxyhexane-$\beta\beta\epsilon\epsilon$-tetracarboxylate, obtained in only small yield from the fraction, b. p. 230—240°/13 mm., formed by the condensation of monochloromethyl ether with the sodium derivative of ethyl butane-$\alpha\alpha\delta\delta$-tetracarboxylate, forms prisms, m. p. 92—93°, and is hydrolysed by concentrated hydrochloric acid to *$\Delta^{\alpha\epsilon}$-hexadiene-$\beta\epsilon$-dicarboxylic acid*, woolly needles, m. p. 180—181°, which yields a caseous *silver* salt. The main product of the condensation consists of an inseparable mixture, b. p. 225°/13 mm., of the preceding ester with ethyl butane-$\alpha\alpha\delta\delta$-tetracarboxylate.

Ethyl ζ-methoxyhexane-$\alpha\alpha\epsilon\epsilon$-tetracarboxylate, prepared from monochloromethyl ether and ethyl pentane-$\alpha\alpha\epsilon\epsilon$-tetracarboxylate, could not be separated from unchanged ester. The mixture, b. p. 220—222°/5 mm., is hydrolysed by hydrochloric acid to pimelic acid and *$\Delta^{\alpha\epsilon}$-hexene-$\beta\zeta$-dicarboxylic acid*, small plates, m. p. 77—79°, the constitution of which has been proved by its oxidation to adipic acid. F. B.

Formaldehyde Salts. HARTWIG FRANZEN and LUDWIG HAUCK (*J. pr. Chem.*, 1915, [ii], **91**, 261—284).—When freshly precipitated lead hydroxide is shaken for twenty-four hours with strong aqueous formaldehyde, it yields a *lead* salt, $C_5H_{16}O_{14}Pb_6$, as a snow-white powder, having a strong odour of formaldehyde. The salt decomposes

when kept for several weeks or when heated at 140°, the formaldehyde content sinking considerably below the original value. The authors assign to this salt the composition represented in formula II, and explain its formation by the alternate condensation of formaldehyde and lead hydroxide with the compound I, as shown in the following scheme: $CH_2(OH)_2 + 2Pb(OH)_2 = 2H_2O + (I.)\ CH_2(O{\cdot}Pb{\cdot}OH)_2 \xrightarrow{CH_2(OH)_2}$ $CH_2(O{\cdot}Pb{\cdot}O{\cdot}CH_2{\cdot}OH)_2 \xrightarrow{Pb(OH)_2} CH_2(O{\cdot}Pb{\cdot}O{\cdot}CH_2{\cdot}O{\cdot}Pb{\cdot}OH)_2 \longrightarrow$ (II.) $CH_2(O{\cdot}Pb{\cdot}O{\cdot}CH_2{\cdot}O{\cdot}Pb{\cdot}O{\cdot}CH_2{\cdot}O{\cdot}Pb{\cdot}OH)_2,2H_2O$.

The *calcium* salt, $Ca(O{\cdot}CH_2{\cdot}OH)_2$, prepared from calcium hydroxide and formaldehyde in strong aqueous solution, undergoes partial decomposition when shaken with water or alcohol; on account of this instability in the presence of water, the composition of the salt depends on the concentration of the formaldehyde solution used in its preparation.

The *strontium* salt, $CH_2(O{\cdot}Sr{\cdot}O{\cdot}CH_2{\cdot}OH)_2$, separates with $7H_2O$, and is much less stable than the calcium salt; the *barium* salt is so unstable that its isolation was impossible; the *magnesium* salt could not be obtained in a pure condition.

The *zinc*, $CH_2(O{\cdot}Zn{\cdot}OH)_2,2H_2O$, *cadmium*,

$CH_2(O{\cdot}Cd{\cdot}O{\cdot}CH_2{\cdot}O{\cdot}Cd{\cdot}O{\cdot}CH_2{\cdot}O{\cdot}Cd{\cdot}OH)_2,9H_2O$,

and green *cupric*, $Cu(O{\cdot}CH_2{\cdot}O{\cdot}Cu{\cdot}O{\cdot}CH_2{\cdot}OH)_2,2H_2O$, salts were prepared by the addition of the metallic sulphates to an aqueous solution of formaldehyde and sodium hydroxide.

With the exception of the cupric compound, all the above salts form colourless or white powders, having a strong odour of formaldehyde.

Attempts to prepare the nickel, iron, aluminium, and sodium salts were unsuccessful.

In view of the formation of the above salts, the authors consider that in the condensation of formaldehyde to sugars under the influence of calcium and other metallic hydroxides, formaldehyde salts of the type $OH{\cdot}CH_2{\cdot}O{\cdot}Ca{\cdot}OH$ are formed as intermediate products, which then undergo condensation with the formation of the calcium salts of glycollaldehyde, glyceraldehyde, and finally of hexoses as illustrated in the following scheme:

$2OH{\cdot}CH_2{\cdot}O{\cdot}Ca{\cdot}OH \longrightarrow Ca(OH)_2 + OH{\cdot}CH_2{\cdot}CH(OH){\cdot}O{\cdot}Ca{\cdot}OH$

$\xrightarrow{OH{\cdot}CH_2{\cdot}O{\cdot}Ca{\cdot}OH.} Ca(OH)_2 + OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}O{\cdot}Ca{\cdot}OH.$

F. B.

Preparation of Acetaldehyde from Acetylene. Chemische Fabrik Griesheim-Elektron (Fr. Pat. 474246; from *J. Soc. Chem. Ind.*, 1915, **34**, 735).—Acetaldehyde is produced by passing excess of acetylene through hot moderately concentrated acids, such as sulphuric (20—25%), phosphoric (30—35%), or organic sulphonic acids, containing mercury salts. The temperature of the acid must be high enough for the aldehyde to be continuously carried forward by the excess of acetylene into absorption vessels containing a suitable solvent, such as water, from which the aldehyde is afterwards recovered by distillation. The use of concentrated acids diminishes the rate of the reduction of the mercury salts to metallic mercury. G. F. M.

Inversion of Sucrose Solutions with Aspartic Acid. L. RADLBERGER and W. SIEGMUND (*Chem. Zentr.*, 1914, ii, 396; from *Oesterr.-ung. Zeitsch. Zucker-Ind.*, 1914, **43**, 418—424).—Calculations based on the values previously obtained for the inversion of sucrose with aspartic acid (A., 1914, i, 930) show that the reaction in this case, as with other acids, follows the Guldberg-Waage law. G. F. M.

Behaviour of Starch "Iodide" towards the Pukall Earthenware Cell and Vanino's Reagent. L. VANINO and A. SCHINNER (*Arch. Pharm.*, 1915, **253**, 47—51).—Solutions of the common starches and also glycogen and inulin penetrate the Pukall cell, the "iodides," however, do not do so. Vanino's reagent (freshly precipitated barium sulphate) carries down the "iodides" completely, but only removes the starches with difficulty and incompletely. Barium sulphate also carries down iodine from an aqueous solution, but not from a solution in an organic solvent; the former solution is, therefore, colloidal.

J. C. W.

Pectin. TH. VON FELLENBERG (*Chem. Zentr.*, 1914, ii, 942—943; from *Mitt. Lebensmittelunters. Hyg.*, **5**, 225—256).—Protopectin occurs as an insoluble substance in unripe and in ripe fruits, and during ripening changes to pectin; the same change occurs when protopectin is boiled with water or dilute acids. The pectin in protopectin is probably not combined with calcium, or any other metal.

Pectin occurs in the sap of fruits and forms colloidal solutions precipitated by alcohol. It contains methyl alcohol as well as arabinose, galactose, and methylpentoses; orange pectin contains araban, 36·1; methylpentosan, 6·0; galactan, 49·3, and methyl alcohol, 11·5%.

The pectin precipitates obtained with salts are not metallic salts, but are probably due to electrolytic coagulation.

Pectic acid is a feeble acid, which, however, liberates carbon dioxide from carbonates, It forms a white powder, the solubility of which is influenced by even small amounts of impurities, especially electrolytes.

N. H. J. M.

The Nature of Humic Acid. II. SVEN ODÉN (*Arkiv. Kem. Min. Geol.*, 1914, **5**, No. 15, 1—13).—Using the method previously described (A., 1912, i, 336), the author has investigated the action of ammonia on aqueous suspensions of humified sphagnum peat, humified foliage peat, and previously dried and well-washed sphagna. Absorption of ammonia takes place, accompanied by strong salt formation in the case of the peats; salt-formation with the sphagna is relatively unimportant. In agreement with the results previously obtained (*loc. cit.*), the existence of one or more acids in humus is considered to be proved.

Ehrenberg and Bahr's paper (A., 1914, i, 50) is replied to.

T. S. P.

Mercurihaloids. F. CALZOLARI and U. TAGLIAVINI (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 925—932).—The authors have investigated

the additive compounds formed by hexamethylenetetramine with double compounds of mercuric haloids with haloids of lithium, magnesium, manganese, cobalt, and nickel. All of these compounds contain 2 mols. of hexamethylenetetramine, the lithium compounds containing 8 mols. of water and the others 10 mols. They are only sparingly soluble, crystallise well, and are stable in the air. The double compounds thus isolated in combination with hexamethylenetetramine are of two types: $[HgX_3]M'$ and $[HgX_4]M'_2$, in some instances only one and in others both of these types appearing.

The following compounds were prepared and analysed:

$2LiCl,HgCl_2,8H_2O,2C_6H_{12}N_4$; $2LiBr,HgBr_2,8H_2O,2C_6H_{12}N_4$; $2LiI,HgI_2,8H_2O,2C_6H_{12}N_4$; $MgCl_2,2HgCl_2,10H_2O,2C_6H_{12}N_4$; $MgBr_2,2HgBr_2,10H_2O,2C_6H_{12}N_4$; $MgI_2,HgI_2,10H_2O,2C_6H_{12}N_4$; $MgI_2,2HgI_2,10H_2O,2C_6H_{12}N_4$; $MnCl_2,2HgCl_2,10H_2O,2C_6H_{12}N_4$; $MnBr_2,2HgBr_2,10H_2O,2C_6H_{12}N_4$; $MnI_2,HgI_2,10H_2O,2C_6H_{12}N_4$; $MnI_2,2HgI_2,10H_2O,2C_6H_{12}N_4$; $CoCl_2,2HgCl_2,10H_2O,2C_6H_{12}N_4$; $CoBr_2,2HgBr_2,10H_2O,2C_6H_{12}H_4$; $CoI_2,HgI_2,10H_2O,2C_6H_{12}N_4$; $NiCl_2,2HgCl_2,10H_2O,2C_6H_{12}N_4$; $NiBr_2,2HgBr_2,10H_2O,2C_6H_{12}N_4$; $NiI_2,HgI_2,10H_2O,2C_6H_{12}N_4$. T. H. P.

Quaternary Salts of Hexamethylenetetramine. V. Monohalogenacetyl Derivatives of Amino-alcohols and the Hexamethylenetetramine Salts Derived Therefrom. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Biol. Chem.*, 1915, **21**, 403—437).—In this paper the authors describe the preparation of the *N* chloroacetyl derivatives of a number of primary and secondary aliphatic and aromatic amino-alcohols, $CH_2Cl\cdot CO\cdot NR'\cdot R\cdot OH$, and the additive compounds which these derivatives form with hexamethylenetetramine. The chloroacetylamino-alcohols, all of which were prepared by the interaction of chloroacetyl chloride and the free amino-alcohols in the presence of aqueous sodium hydroxide, have been converted into esters of the general formula $CH_2Cl\cdot CO\cdot NR'\cdot R\cdot O\cdot COR''$ by the addition of the acid chloride, $R''\cdot COCl$, dissolved in chloroform to a well cooled solution of the chloroacetylamino-alcohol in pyridine.

The hexamethylenetetramine derivatives of the chloroacetylamino-alcohols and their esters were all prepared by boiling equimolecular amounts of the components in chloroform solution.

Chloroacetylaminomethyl alcohol yields a hexamethylenetetramine compound which has m. p. 154—155° (decomp.), and is not hygroscopic (compare Einhorn and Göttler, A., 1908, i, 608); the *benzoate*, $CH_2Cl\cdot CO\cdot NH\cdot CH_2\cdot OBz$, forms prismatic rods, m. p. 73—73·5° (corr.) with slight preliminary softening; the p-*methoxybenzoate*, large rosettes of delicate hairs, m. p. 106—107° (corr.) with slight preliminary sintering. Attempts to prepare the hexamethylenetetramine salts of the two last-mentioned esters by the usual methods resulted only in isolation of the impure quaternary salt of chloroacetylaminomethyl alcohol.

β-Chloroacetylaminoethyl alcohol, $CH_2Cl\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot OH$, has b. p. 141—145° (corr.)/0·25—0·35 mm., solidifies in a freezing mixture, and is converted by sodium iodide in acetone solution at the ordinary

temperature into *β-iodoacetylaminoethyl alcohol* (not obtained in a pure condition), which forms additive *compounds* with hexamethylenetetramine, m. p. 142—143° (decomp.), and trimethylamine, $C_7H_{17}O_2N_2I$, m. p. 138—139° (corr.), with previous sintering at 135°.

β-Chloroacetylaminoethyl benzoate, $OBz\cdot CH_2\cdot CH_2\cdot NH\cdot CO\cdot CH_2Cl$, prepared by the Schotten-Baumann method (1) from β-chloroacetylaminoethyl alcohol and benzoyl chloride; (2) from β-aminoethyl benzoate hydrobromide and chloroacetyl chloride, forms flat needles, softening at 68·5°, m. p. 69—69·5° (corr.), and yields a hexamethylenetetramine *compound*, m. p. 162° (decomp.), with previous darkening at 158°. The following β-chloroacetylaminoethyl esters were obtained from β-chloroacetylaminoethyl alcohol and the requisite acid chloride in pyridine solution:

o-*Toluate*, $C_6H_4Me\cdot CO_2\cdot CH_2\cdot CH_2\cdot NH\cdot CO\cdot CH_2Cl$, faintly pink clusters of spears, softening at 64·5°, m. p. 65—65·5° (corr.); hexamethylenetetramine *compound*, m. p. 168° (decomp.).

p-*Toluate*, glistening, felted hairs, m. p. 106—107·5° (corr.); the hexamethylenetetramine *compound* melts at 161—162° to an orange liquid when rapidly heated, but at a much lower temperature when slowly heated.

β-Naphthoate, minute, voluminous, triboelectric needles, m. p. 137—139° (corr.); hexamethylenetetramine *compound*, m. p. 174—176° (decomp.).

o-*Nitrobenzoate*, syrup; the hexamethylenetetramine *compound* crystallises with chloroform (1 mol.), which is retained even on heating under diminished pressure at the temperature of boiling alcohol, but may be removed by boiling with acetone; free from chloroform it has m. p. 174° (decomp.).

The m-*nitrobenzoate*, not isolated in a pure condition, yields a hexamethylenetetramine *compound*, $C_{17}H_{23}O_5N_6Cl$.

The p-*nitrobenzoate*, long, prismatic needles, m. p. 127—128° (corr.), yields a hexamethylenetetramine *compound*, m. p. 182—182·5° (decomp.), and an additive *compound* with trimethylamine, $C_{14}H_{20}O_5N_3Cl$, white, crystalline powder, m. p. 175—176° (corr.); it is reduced by stannous chloride and hydrogen chloride in glacial acetic acid solution to the p-*aminobenzoate*, which forms pale cream-coloured, minute spindles, m. p. 117—118·5° (corr.) with preliminary softening, and after diazotisation in hydrochloric acid solution couples with diethylaniline to form *β-chloroacetylaminoethyl 4-diethylaminobenzene-p-azobenzoate*, $NEt_2\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2\cdot NH\cdot CO\cdot CH_2Cl$; this forms red, microscopic rosettes of platelets, sintering at 111°, is completely fused at 116°, and yields a hexamethylenetetramine *compound*, light orange crystals, m. p. 179—181°.

o-*Acetoxybenzoate*, $OAc\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2\cdot NH\cdot CO\cdot CH_2Cl$, glistening, snow-white tablets, m. p. 117° (corr.) with preliminary softening; hexamethylenetetramine *compound*, micro-platelets, m. p. 154—156° (decomp.).

p-*Methoxybenzoate*, rosettes of needles, m. p. 96·5—97° (corr.) with slight preliminary softening; hexamethylenetetramine *compound*, m. p. 153—154° (decomp.).

Cinnamate, delicate, glistening needles, m. p. 120—122° (corr.).

β-Chloroacetylaminodiethyl ether, $CH_2Cl{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}OEt$, prepared from β-aminodiethyl ether and chloroacetyl chloride in aqueous sodium hydroxide, has b. p. 132°(corr.)/15 mm., and forms a very hygroscopic hexamethylenetetramine *compound*, m. p. 135—145°.

o-*Tolyl β-aminoethyl ether*, $C_6H_4Me{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, obtained from *o*-tolyl β-bromoethyl ether and alcoholic ammonia at 120°, has b. p. 128°(corr.)/19 mm. and yields a N-*chloroacetyl* derivative, which crystallises in minute prisms, softening at 39°, m. p. 39·5—40·5° (corr.), b. p. 168—169°/0·7 mm., and forms a hexamethylenetetramine *compound*, m. p. 162° (decomp.).

β-Chloroacetylethylaminoethyl alcohol, $CH_2Cl{\cdot}CO{\cdot}NEt{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, from ethylaminoethyl alcohol, is a pale yellow, viscid oil, b. p. 130—135°/0·6 mm.; the p-*nitrobenzoate*,

$$CH_2Cl{\cdot}CO{\cdot}NEt{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2,$$

crystallises in colourless, minute rhombs, m. p. 73·5—74° (corr.) with slight preliminary softening, and yields a hexamethylenetetramine *compound*, m.p. 154—155°, to an orange liquid.

β-Chloroacetylphenylaminoethyl alcohol,

$$CH_2Cl{\cdot}CO{\cdot}NPh{\cdot}CH_2{\cdot}CH_2{\cdot}OH,$$

prepared from β-phenylaminoethyl alcohol, forms prisms, m. p. 67·5—68·5° (corr.) with preliminary softening; the p-*nitrobenzoate*, $CH_2Cl{\cdot}CO{\cdot}NPh{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2$, crystallises in faintly yellow spears, m. p. 115—116° (corr.) with slight preliminary softening and yields a hexamethylenetetramine *compound*, melting at 167—168° to an orange paste.

β-Bromoacetylphenylaminoethyl alcohol, obtained together with a *substance*, m. p. 131—133°, by the interaction of bromoacetyl bromide and β-phenylaminoethyl alcohol in cold benzene solution, forms rhombic crystals, m. p. 58—60° (corr.).

p-*Dimethylamino-β-phenylaminoethyl alcohol*,

$$NMe_2{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}OH,$$

prepared by boiling a mixture of *p*-aminodimethylaniline, ethylene chlorohydrin and water for two hours, forms hygroscopic, almost colourless aggregates of irregular plates, m. p. 32·5—35° (corr.), b. p. 215—217°/16 mm., and yields a N-*chloroacetyl* derivative in colourless rhombs, m. p. 85·5—87° (corr.) with preliminary softening.

p-*Methoxy-β-phenylaminoethyl alcohol*, obtained in a similar manner from *p*-anisidine, has m. p. 43·5—44·5° (corr.), b. p. 188—191°/8 mm.

p-*Nitrobenzo-γ-bromopropylamide*, $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_3H_6Br$, prepared by the gradual addition of aqueous sodium hydroxide with constant shaking to a well-cooled mixture of *p*-nitrobenzoyl chloride in benzene and aqueous γ-bromopropylamine hydrobromide, crystallises in minute, colourless needles, m. p. 107·5—108° (corr.) with slight preliminary softening, and is transformed by heating on the water-bath in aqueous solution into *γ-aminopropyl* p-*nitrobenzoate hydrobromide*, $NO_2{\cdot}C_6H_4{\cdot}CO_2{\cdot}C_3H_6{\cdot}NH_2,HBr$, from which the free *ester* is liberated, by the action of aqueous sodium hydroxide, as an oil and then gradually undergoes rearrangement into p-*nitrobenzo-γ-hydroxypropylamide*, $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_3H_6{\cdot}OH$. The latter compound

crystallises in heavy, rhombic prisms, m. p. 102·5—103·5° (corr.), and when boiled with chloroacetic anhydride in chloroform solution is converted into γ-p-*nitrobenzoylaminopropyl chloroacetate*,

$$CH_2Cl\cdot CO_2\cdot C_3H_6\cdot NH\cdot CO\cdot C_6H_4\cdot NO_2,$$

faintly yellow, crystalline aggregates, m. p. 93—106°.

γ-Chloroacetylaminopropyl p-*nitrobenzoate*,

$$NO_2\cdot C_6H_4\cdot CO_2\cdot C_3H_6\cdot NH\cdot CO\cdot CH_2Cl,$$

prepared from γ-aminopropyl *p*-nitrobenzoate and chloroacetyl chloride in the presence of aqueous sodium hydroxide at a low temperature, forms aggregates of flat needles, m. p. 78—79°, and yields a hexamethylenetetramine *compound*, m. p. 178—179°, with preliminary darkening.

γ-Chloroacetylaminopropyl p-*methoxybenzoate*, obtained in a similar manner from γ-aminopropyl *p*-methoxybenzoate, crystallises in faintly pink, radiating masses of delicate hairs, softening at 172°, m. p. 72·5—73° (corr.), and forms a hexamethylenetetramine *compound*, crystallising in glistening leaflets, m. p. 167—168°, to an orange liquid.

*β-Chloroacetylamino*isopropyl *alcohol*,

$$CH_2Cl\cdot CO\cdot NH\cdot CH_2\cdot CHMe\cdot OH,$$

from β-amino*iso*propyl alcohol (Gabriel and Meymann, A., 1890, 1266) has m. p. 33—34·5° (corr.), b. p. 131—132°(corr.)/0·6 mm., and yields a hexamethylenetetramine *compound* (decomp. 171—172°); the p-*nitrobenzoate*, $NO_2\cdot C_6H_4\cdot CO_2\cdot CHMe\cdot CH_2\cdot NH\cdot CO\cdot CH_2Cl$, crystallises in faintly yellow, silky needles, m. p. 133·5—134·5° (corr.) with slight preliminary softening, and forms a hexamethylene *compound*, faintly yellow plates, darkening above 170°, m. p. 180—182° (decomp.).

*β-Amino*isopropyl p-*nitrobenzoate hydrobromide*,

$$NO_2\cdot C_6H_4\cdot CO_2\cdot CHMe\cdot CH_2\cdot NH_2,HCl,$$

obtained hy boiling *β-p*-nitrobenzoylamino*iso*propyl bromide (Uedinck, A., 1899, i, 497) with water until completely dissolved, has m. p. 221—222°, and is converted by aqueous alkali into p-*nitrobenzo-β-hydroxy*-n-*propylamide*, $NO_2\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CHMe\cdot OH$, glistening platelets, m. p. 168—169°, and not the free amino*iso*propyl ester as stated by Uedinck.

β-p-*Nitrobenzoylamino*isopropyl *chloroacetate*,

$$CH_2Cl\cdot CO_2\cdot CHMe\cdot CH_2\cdot NH\cdot CO\cdot C_6H_4\cdot NO_2,$$

prepared from the preceding amide by heating with chloroacetyl chloride in chloroform solution, crystallises in almost colourless plates and prisms, m. p. 89—94° (corr.), and yields a hexamethylenetetramine *compound*, m. p. 175—178°.

δ-*Chloroacetylamino*-n-*butanol*, $CH_2Cl\cdot CO\cdot NH\cdot C_4H_8\cdot OH$, m. p. 30° (corr.), b. p. 165—167°(corr.)/0·7 mm., forms a hygroscopic hexamethylenetetramine *compound*, sintering at 122°, m. p. 125°; the p-*nitrobenzoate*, $NO_2\cdot C_6H_4\cdot CO_2\cdot C_4H_8\cdot NH\cdot CO\cdot CH_2Cl$, crystallises in almost white rosettes of minute prisms, m. p. 79° (corr.), and yields a hexamethylenetetramine *compound*, thick, faintly yellow plates, darkening above 165°, m. p. 170—172° (decomp.).

β-Chloroacetylamino-γ-*butanol*, $OH\cdot CHMe\cdot CHMe\cdot NH\cdot CO\cdot CH_2Cl$, has m. p. 38—39° (corr.), b. p. 119°(corr.)/0·3 mm., and forms a hexamethylenetetramine *compound*, m. p. 167—169°; the p-*nitrobenzoate*,

$NO_2 \cdot C_6H_4 \cdot CO_2 \cdot CHMe \cdot CHMe \cdot NH \cdot CO \cdot CH_2Cl$, crystallises in pale cream-coloured rosettes of delicate leaflets, m. p. 117—118° (corr.), and yields a hexamethylenetetramine *compound*, colourless micro-crystals, m. p. 189—191° (decomp.).

γ-Chloroacetylamino-β-pentanol, $OH \cdot CHMe \cdot CHEt \cdot NH \cdot CO \cdot CH_2Cl$, is a waxy solid, m. p. 52—60°, b. p. 126—128°/0·3 mm., and forms a hygroscopic hexamethyltetramine *compound*, m. p. 167—168° (decomp.) with preliminary darkening,

α-Chloroacetylamino-β-methyl-β-butanol,

$$OH \cdot CMeEt \cdot CH_2 \cdot NH \cdot CO \cdot CH_2Cl,$$

has b. p. 134°(corr.)/0·7 mm.; the hygroscopic hexamethylenetetramine *compound* has m. p. 170° (decomp.).

γ-Chloroacetylamino-β-methyl-β-butanol,

$$OH \cdot CMe_2 \cdot CHMe \cdot NH \cdot CO \cdot CH_2Cl,$$

b. p. 122°(corr.)/0·4 mm., yields a hexamethylenetetramine *compound*, m. p. 174—175° (decomp.).

β-Hydroxy-β-phenylethylamine, prepared by reducing benzaldehyde cyanohydrin with sodium amalgam in alcoholic solution, keeping the mixture just acid with acetic acid (compare D.R.-P. 193634), forms a N-*chloroacetyl* derivative, $OH \cdot CHPh \cdot CH_2 \cdot NH \cdot CO \cdot CH_2Cl$, which crystallises in thick plates, softening at 108°, m. p. 109—109·5° (corr.), and yields a hexamethylenetetramine *compound*, m. p. 179° (decomp.).

β-Hydroxy-β-p-tolylethylamine, $C_6H_4Me \cdot CH(OH) \cdot CH_2 \cdot NH_2$, obtained in a similar manner from *p*-tolualdehyde cyanohydrin, forms snow-white crystals, m. p. 68—69° (corr.); the N-*chloroacetyl* derivative crystallises in thick, colourless plates or prisms, m. p. 81—82° (corr.) with preliminary softening. The preparation of *β-hydroxy-β-p-methoxyphenylethylamine* from anisaldehyde cyanohydrin is also described.

β-Hydroxy-αβ-diphenylethylamine (Erlenmeyer, A., 1899, i, 760) yields with chloroacetic anhydride in benzene solution a N-*chloroacetyl* derivative, $OH \cdot CHPh \cdot CHPh \cdot NH \cdot CO \cdot CH_2Cl$, which crystallises in interlaced, hair-like needles, m. p. 194—194·5° (corr.), and forms a hexamethylenetetramine *compound*, crystallising with chloroform in hexagonal platelets; after removal of the chloroform at 100° under diminished pressure, the compound has m. p. 174° (decomp.).

The N-*chloroacetyl* derivative of *iso*-β-hydroxy-αβ-diphenylethylamine (Erlenmeyer, *loc. cit.*), prepared in a similar manner, forms colourless needles, m. p. 156—157° (corr.), and yields a hexamethylenetetramine compound, m. p. 197—199° (decomp.). F. B.

Quaternary Salts of Hexamethylenetetramine. VIII. Miscellaneous Substances Containing Aliphatically Bound Halogen and the Hexamethylenetetraminium Salts Derived Therefrom. Walter A. Jacobs and Michael Heidelberger (*J. Biol. Chem.*, 1915, **21**, 465—475).—An account of the preparation of a number of substances, which could not be logically incorporated in the previous papers.

β-Hydroxyethylhexamethylenetetraminium iodide, prepared from ethylene iodohydrin, crystallises in needles, m. p. 157° (decomp.).

γ-Chloropropylhexamethylenetetraminium bromide, from trimethylene

chlorobromide, forms irregular micro-prisms, which turn yellow above 140°, m. p. 180—183° (decomp.); *γ-hydroxypropylhexamethylenetetraminium iodide*, from trimethylene iodohydrin; *cetylhexamethylenetetraminium iodide*, softens at 131° and melts gradually up to 157°, with evolution of gas.

β-Phenylethyl iodide, prepared from the chloride (Barger, T., 1909, **95**, 2194) and sodium iodide in acetone solution, has b. p. 104·5—130·5°/28 mm., and forms a hexamethylenetetramine *compound*, crystallising in pale yellow cubes, m. p. 159° (decomp.).

o-*Iodobenzylhexamethylenetetraminium bromide* effervesces and turns yellow at 173—175°.

β-Carbethoxyethylhexamethylenetetraminium iodide, from ethyl β-iodopropionate, crystallises in glistening leaflets, m. p. 137—138° (decomp.).

sec.-*Octyl bromoacetate* has b. p. 137° (corr.)/18 mm., and forms a gelatinous hexamethylenetetramine *compound*.

The additive *compound* of hexamethylenetetramine with bornyl bromoacetate has m. p. 178—181° (sintering at 170°); with menthyl bromoacetate, m. p. 153—154°; with phenyl bromoacetate, m. p. 149—150°.

Tribromo-p-*tolyl bromoacetate*, prepared from tribromo-*p*-cresol and bromoacetyl bromide in aqueous sodium hydroxide solution, forms cream-coloured prisms, softening at 60°, m. p. 60·5—61·5° (corr.).

o-*Nitrophenyl bromoacetate*, m. p. 55·5—56° (corr.), yields a hexamethylenetetramine *compound*, greyish micro-prisms, m. p. 149—150°.

The *chloroacetyl* derivatives of 1-benzeneazo-2-naphthol forms orange, felted needles, m. p. 127—128° (corr.).

β-Hydroxyethyl p-*methoxybenzoate*, from ethylene glycol and anisoyl chloride in pyridine solution, has b. p. 149—150° (corr.)/0·4 mm., and reacts with chloroacetyl chloride in benzene solution, yielding *β-chloroacetoxyethyl* p-*methoxybenzoate*,

$$CH_2Cl\cdot CO_2\cdot CH_2\cdot CH_2\cdot O\cdot CO\cdot C_6H_4\cdot OMe,$$

b. p. 170—175°/0·5 mm., m. p. 45·5—46·5° (corr.), which forms a hygroscopic hexamethylenetetramine *compound*, softening at 70°, and gradually melting below 90°.

Ethylene dianisate, obtained as a by-product in the preparation of β-hydroxyethyl *p*-methoxybenzoate, crystallises in prisms, m. p. 117—117·5°, with slight preliminary softening.

ω-*Chloroacetylaminoacetophenone*, $CH_2Cl\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot C_6H_5$, crystallises in micaceous scales, m. p. 124—126·5° with preliminary softening; the hexamethylenetetramine *compound* forms microplatelets having a faint yellowish-green tinge, m. p. 149—150° (decomp.).

Chloroacetylamino-4 : 4′-*tetramethyldiaminodiphenylmethane*,

$$CH_2Cl\cdot CO\cdot NH\cdot CH(C_6H_4\cdot NMe_2)_2,$$

prepared from leucoauramine and chloroacetyl chloride, crystallises in colourless plates and needles, melting at 164—164·5° (corr.) to a deep-green liquid; the hexamethylenetetramine *compound* has m. p. 175° (decomp. 179°).

Chloroacetotriphenylmethylamide, $CH_2Cl\cdot CO\cdot NH\cdot CPh_3$, forms snow-white, interlaced hairs, m. p. 201—202·5° (corr.), and yields a hexa-

methylenetetramine *compound* which crystallises in small, transparent cubes, m. p. 194—195° (decomp.), after turning yellow at 150°.

β-Acetyl-*α*-chloroacetyl-*α*-phenylhydrazine forms a hexamethylenetetramine *compound*, long, silky needles, m. p. 192—193°.

β-Chloroacetyl-α-phenyl-α-benzylhydrazide, prepared from *α*-phenyl-*α*-benzylhydrazine, has m. p. 112·5—113·5°, and yields a hexamethylenetetramine *compound*, m. p. 145—146°. F. B.

The Salting-out of Amino-acids and the Separation of Amino-acids with the Aid of Neutral Salts. P. Pfeiffer and Fr. Wittka (*Ber.*, 1915, **48**, 1041—1047).—It has been shown (Pfeiffer and von Modelski, A., 1912, i, 949; 1913, i, 709) that the simple amino-acids and the polypeptides possess the property of forming additive compounds with neutral salts; such compounds can be used for the separation of amino-acids, and the influence of neutral salts on the solubility of amino-acids (A., 1912, i, 949) can be applied to the same object.

It is observed that glycine, tyrosine, and aspartic acid are not precipitable by salts, whereas alanine can be caused to separate to a slight extent by ammonium sulphate solutions, whilst *dl*-leucine and *dl*-phenylalanine are precipitated to a much more considerable extent. Ammonium sulphate was found to have the most marked effect, but sodium and potassium chlorides, sodium and magnesium sulphates, sodium and potassium acetates, and potassium oxalate were also effective. The amino-acids under these conditions separate in the free state, and the varying ease with which the amino-acids are salted-out permits the separation of such pairs as glycine and phenylalanine, *l*-leucine and glycine in this way.

The additive compounds of calcium chloride with glycine and *d*- or *dl*-alanine are very soluble in water, but a marked difference exists between the solubilities of the compounds in aqueous alcohol, the glycine compound being sparingly soluble in this solvent. It is thus possible to effect a satisfactory separation of these amino-acids. As copper glycine gives a blue *compound*, $CaCl_2,(NH_2\cdot CH_2\cdot CO_2)_2Cu,3H_2O$, with calcium chloride, the compound being very soluble in water, it is necessary to free the glycine-calcium chloride compound from calcium chloride before attempting to convert it into copper-glycine.

D. F. T.

Anhydrides and Amines from α-Amino-acids. II. F. Graziani (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 936—941).—The results obtained by heating certain *α*-amino-acids with glycerol or with hydrocarbons (*ibid.*, 822) support Balbiano's view that the intervention of glycerol is unnecessary for the anhydrification of *α*-amino-acids. Confirmatory results have now been obtained with leucine, tyrosine, and cystine, which were heated with glycerol or with diphenylmethane.

T. H. P.

Preparation of Glutamic Acid and Betaine from Molasses Residues. K. Andrlík (*Zeitsch. Zuckerind. Böhm.*, 1915, **39**, 387—391).—The concentrated residue (1 kilo.) is treated with 450 grams

of tartaric acid in 30% solution. After one hour it is filtered from the potassium tartrate, evaporated down to about 15° Bg., and crystals of glutamic acid added. In about twelve hours the glutamic acid crystallises out. The acid is recrystallised twice, the second time with a little blood charcoal. The yield is about 60 grams. Instead of tartaric acid, sulphuric or phosphoric acid may be employed. The yield of glutamic acid is then, however, only about 30 grams.

To obtain betaine, the residues, treated with phosphoric acid as already described, are left for forty-eight hours, filtered from the mixed crystals of potassium phosphate and glutamic acid, treated with a further 300 c.c. of 40% phosphoric acid, and evaporated down until the weight is about 800 grams. After forty-eight hours, it is filtered from the crude betaine phosphate (160—190 grams) which separates. It is desirable to obtain the phosphate in as pure a state as possible before preparing the free betaine. The phosphate (100 grams) is dissolved in 750 c.c. of warm water, treated with about 20 grams of slaked lime, as milk of lime (D about 1·035), until alkaline, filtered from calcium phosphate, and evaporated until crystals begin to form. The yield of pure betaine is about 7% of the molasses residue.

N. H. J. M.

Xylohexosamic Acid, its Derivatives and their Bearing on the Configuration of *iso*Saccharic and Epi*iso*saccharic Acids. P. A. Levene and F. B. La Forge (*J. Biol. Chem.*, 1915, **21**, 351—359. Compare this vol., i, 601).—On successive treatment with ammonia and hydrocyanic acid, and subsequent hydrolysis of the resulting nitrile, *l*-xylose yields a *l*-xylohexosamic acid, which is converted by deamination and oxidation into an $\alpha\delta$-anhydrotetrahydroxyadipic acid. From the method of preparation it follows that the amino-acid has the configuration of either *l*-glucosamic acid or *l*-idosamic acid, whilst the anhydro-acid is either *l*-$\alpha\delta$-anhydrosaccharic acid or *l*-$\alpha\delta$-anhydroidosaccharic acid.

The configuration of the amino-acid has been determined from the following considerations. Of the four hexosamic acids corresponding to the *l*-saccharic acid series, *l*-glucosamic and *l*-glucosamic acids will give rise to the same $\alpha\delta$-anhydrosaccharic acid, whilst *l*-mannosamic and *l*-idosamic acids will yield different anhydro-acids, namely, anhydromannosaccharic and anhydroidosaccharic acids. If the anhydro-acid, obtained from *l*-xylohexosamic acid, has the configuration of $\alpha\delta$-anhydrosaccharic acid, it must be identical in all respects with the exception of the sign of its rotation with one of the anhydro-acids, *iso*saccharic and epi*iso*saccharic acid, derived from *d*-glucosamine. It is found, however, that the anhydro-acid differs in m. p., magnitude of its rotation, and in the properties of its potassium hydrogen salt from either of these acids, and therefore has the configuration of $\alpha\delta$-anhydro-idosaccharic acid.

The epimeric anhydrotetrahydroxyadipic acid, prepared from the lactone of the above *l*-xylohexosamic acid by successive deamination and oxidation, proved to be identical in all respects, except in the sign of its rotation, with epi*iso*saccharic acid.

The latter acid, therefore, has the configuration of $\alpha\delta$-anhydro-

saccharic acid, whilst *iso*saccharic acid must be αδ-anhydromannosaccharic acid.

From these results it follows that chitose, chitonic and chitaric acids have the configuration of αδ-anhydromannose, αδ-anhydromannonic acid, and αδ-anhydrogluconic acid respectively. l-*Xylohexosamic acid*, $C_6H_{13}O_6N$, prepared by the interaction of *l*-xylosimine and concentrated hydrocyanic acid and subsequent hydrolysis with hydrochloric acid, crystallises in large, colourless prisms, decomp. 235° with previous darkening at 190°, $[\alpha]_D^{30}$ +11·77° after twenty minutes, falling to −3·01° after forty hours. It is converted by alcoholic hydrogen chloride into l-*xylohexosaminolactone hydrochloride*, $C_6H_{12}O_5NCl$, spherical aggregates of prismatic needles or long prisms, m. p. 195° (decomp.), with previous browning at 180°. With benzaldehyde and hydrogen chloride in alcoholic solution, it yields *ethyl* l-*dibenzylidenexylohexosamate hydrochloride*, $C_{22}H_{26}O_6NCl$, m. p. 217°.

On treatment with silver nitrite in hydrochloric acid solution and subsequent oxidation with nitric acid, it is converted into l-αδ-*anhydroidosaccharic acid*, $C_6H_8O_7,2H_2O$, colourless, prismatic needles, m. p. 226° (decomp.), $[\alpha]_D^{20}$ −93·32° (*potassium hydrogen* salt, long, colourless needles), whilst the amino-lactone hydrochloride, when submitted to the same treatment, gives rise to l-αδ-*anhydrosaccharic* (l-*epi*isosaccharic) *acid*, m. p. 163°, which was isolated by successive conversion into the *potassium hydrogen*, $C_6H_7O_7K,H_2O$, $[\alpha]_D^{28}$ −38·09°, and *lead* salts.

F. B.

Methylation of Glucosamic Acid. A Way from Sugar to Betaine. Hans Pringsheim (*Ber.*, 1915, **48**, 1158—1161).—When glucosamic acid is methylated by means of methyl sulphate and barium hydroxide solution, the molecule undergoes fission, the products being betaine and an uncrystallisable solid consisting probably of a methylated tetrose (compare Haworth, T., 1915, **107**, 8). Attention is drawn to the possible connexion of such a reaction with the occurrence of betaine and of proteins in the sugar beet. D. F. T.

New Investigations on Metallicarbamides. G. A. Barbieri (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 916—921. Compare A., 1913, i, 959; this vol., i, 507).—Aluminicarbamide chloride, bromide and nitrate could not be obtained, owing to their excessive solubility, but various other salts have been prepared and are found to be analogous to, and probably isomorphous with, the corresponding salts of chromi-, ferri- and vanadi-carbamide, since aluminicarbamide and vanadicarbamide perchlorates form mixed crystals. The salts of titanicarbamide are highly unstable and soluble, and only the perchlorate has been isolated in the pure state; the existence of the perchloric acid residue, which is a strong oxidising agent, in the same compound as tervalent titanium, which is a powerful reducing agent, furnishes confirmation of the fact that the atom of the metal forms a complex with the carbamide molecules. The following new compounds are described.

Aluminicarbamide perchlorate, $[Al(CON_2H_4)_6](ClO_4)_3$, forms white, microscopic prisms; the *permanganate*, $[Al(CON_2H_4)_6](MnO_4)_3$, forms

black crystals giving a violet solution, and, in the solid state, is soluble in all proportions with the perchlorate; the *dichromate*, $[Al(CON_2H_4)_6]_2(Cr_2O_7)_3$, orange crystals; the *iodide*, $[Al(CON_2H_4)_6]I_3$, white, crystalline powder; the *periodide*, $[Al(CON_2H_4)_6]I_3,3I_2$, crystals of the colour of graphite; the *sulphate periodide*, $[Al(CON_2H_4)_6]SO_4I,I_2$, orange-red crystals; the *nitrate periodide*, $[Al(CON_2H_4)_6](NO_3)_2I,I_2$, red, crystalline powder.

Titanicarbamide perchlorate, $[Ti(CON_2H_4)_6](ClO_4)_3$, forms a stable, lilac powder, and gives a violet aqueous solution, which rapidly loses its colour.

Chromicarbamide persulphate, $[Cr(CON_2H_4)_6]_2(S_2O_8)_3$, forms a greenish-white, crystalline powder, which gradually changes to well-formed, green crystals, and *ferricarbamide persulphate*, $[Fe(CON_2H_4)_6]_2(S_2O_8)_3$, a bluish-green, crystalline powder, giving a yellow aqueous solution.

T. H. P.

Preparation of Carbamides of Brominated Monobasic Fatty Acids. Farbenfabriken vorm. F. Bayer & Co., and Knoll & Co. (D.R.-P. 283105; from *J. Soc. Chem. Ind.*, 1915, **34**, 735).—Symmetrical diacylated carbamides of the formula

$$R{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}R,$$

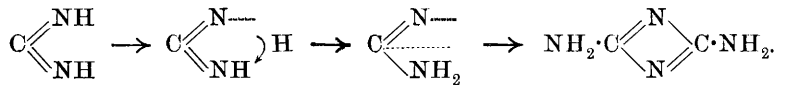
where R·CO is a brominated fatty acid residue, are converted by weak saponifying agents into monoacylated carbamides. Thus, *bis*-bromo-α-ethylbutyrylcarbamide in methyl alcohol gives with aqueous ammonia bromo-α-ethylbutyrylcarbamide, and *bis*-α-bromo*iso*valerylcarbamide suspended in water gives with *N*/1-sodium hydroxide, α-bromo*iso*-valerylcarbamide. G. F. M.

Constitution of Carbamides. II. Relation of Cyanamide to Urea. Constitution of Cyanamide and the Mechanism of its Polymerisation. Emil Alphonse Werner (T., 1915, **107**, 715—728).—The author points out that the properties of cyanamide are characteristic of a tautometric substance, its remarkable stability in aqueous solution being probably due to an electrostatic equilibrium between the acidic form (I) and the basic form (II):

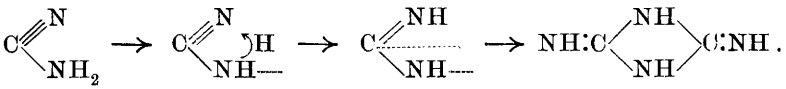
$$(I)\ NH{:}C{:}NH \rightleftharpoons CN{\cdot}NH_2\ (II).$$

The polymerisation by acids and alkalis is explained by the aid of a theory similar to that already employed to account for the polymerisation of cyanic acid (T., 1913, **103**, 1017).

Addition of an acid disturbs the equilibrium by neutralisation of the basic form, and thus causes the acidic form to undergo the changes illustrated in the following scheme:



Alkalis, on the other hand, neutralise the acidic form and induce polymerisation as follows:



Dicyanodiamide, being a perfectly neutral substance, can only be a transition product formed from the cyanamide in its effort to attain equilibrium with the base or acid. In the latter case equilibrium is soon attained by further hydrolysis of the dicyanodiamide to the strongly basic dicyanodiamidine, whilst in the case of the action of bases the diamide is hydrolysed to a strong acid, probably Hallwachs' amidodicyanic acid. Since the acid character of cyanamide is more pronounced than the basic property, a weak base should exert a greater accelerating effect on the polymerisation than a correspondingly weak acid. Experiments carried out with acetic acid and ammonia confirm this view.

The polymerisation of cyanamide to dicyanodiamide by heat alone, and the formation of melamine by heating cyanamide above 200° find a ready explanation on the author's theory.

The behaviour of cyanamide towards nitrous acid is also in agreement with the above view, that cyanamide in solution consists of an equilibrium mixture of the amino- and di-imino- forms.

In the presence of acetic acid, nitrous acid has practically no action on cyanamide, but in the presence of sulphuric about half the theoretical amount of nitrogen required by the equation :

$$CN\cdot NH_2 + HNO_2 = N_2 + H_2 + CN\cdot OH$$

is evolved in the course of two minutes, and this is followed by a very slow evolution of gas, largely composed of carbon dioxide, and mainly due to the gradual hydrolysis of the cyanic acid produced in the first stage. An examination of the residual liquid showed that, after twenty minutes, nearly 60% of the cyanamide was unchanged, whilst, after twenty hours, 13% was still undecomposed. These results show that whilst all the cyanamide present at the outset in the amino-form is rapidly decomposed by nitrous acid in the usual manner, the more stable imino-form changes very slowly at the ordinary temperature into the amino-form, which is then attacked as fast as it is generated. A normal solution of cyanamide contains approximately 60% in the di-imino-form. Contrary to the usual view, cyanamide is a remarkable resistant to hydrolysis; no trace of carbamide could be detected after heating with water or with dilute acids and alkalis. This behaviour is readily explained on comparing the formula of carbamide, $NH{:}C\langle^{NH_2}_{O}$, with that of cyanamide; the relation between the two compounds is evidently not the simple one so generally supposed, namely, that of nitrile and amide.

The hydrolysis of cyanamide to carbamide by means of nitric and hydrochloric acids in moist ethereal solution is also described and discussed from the point of view of the author's theories. F. B.

Halogen Compounds of Molybdenum and Tungsten. X. The Cyanides of Tungsten and Molybdenum. The Valency of the Central Atoms in their Complex Anions. ARTHUR ROSENHEIM and EITEL DEHN (*Ber.*, 1915, **48**, 1167—1178).—The compound $K_3W_2Cl_9$ (Olsson, A., 1913, ii, 328; 1914, i, 504, 944) is conveniently prepared by the action of tin on a solution of potassium

tungstate saturated with hydrogen chloride, a yield of 55% being obtained in two days.

By a process analogous to that used for molybdenum (Rosenheim and Koss, A., 1906, i, 603) the action of sodium paratungstate on sodium thiocyanate in dilute hydrochloric acid followed by the addition of pyridine gave a *compound* $W(OH)_2(SCN)_3,2C_5H_5N$, containing quinquevalent tungsten; this compound dissolves in potassium cyanide solution to a blue solution which turns yellow on warming and can be made to yield a *cadmium* salt, $[Cd(NH_3)_3]_2[W(CN)_8],2H_2O$.

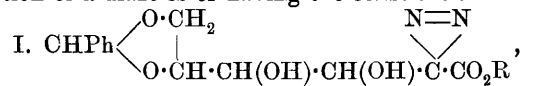
The potassium salt, $K_4W(CN)_8,2H_2O$, when treated with concentrated hydrochloric acid in the cold gives the *acid*, $H_4W(CN)_8,6H_2O$, a yellow, crystalline powder, and reacts with a solution of thallous nitrate, giving yellow needles of the thallium *salt*, $Tl_4W(CN)_8$.

It is shown by experimental evidence that the method of examination with ammoniacal silver nitrate solution is applicable to the compounds of tungsten and molybdenum of lower valency; with this reagent, results were obtained indicating that with the compounds

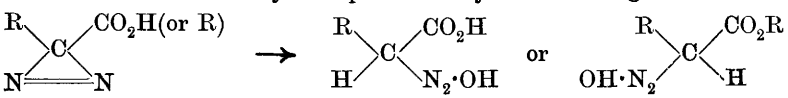
$$K_4W(CN)_8,2H_2O,$$

$K_4Mo(CN)_8,2H_2O$, and $K_4Mo(OH)_4(CN)_4,6H_2O$, even in the presence of additional cyanide ions, the valency of the central metal atom was between 4 and 5, whilst with solutions of the two former which had been oxidised with potassium permanganate solution, the reagent indicated a valency between 5 and 6 (compare Olsson, *loc. cit.*). These abnormal results are attributed to the effect of auxiliary valencies. D. F. T.

The Walden Rearrangement in the Hexoses. P. A. Levene and F. B. La Forge (*J. Biol. Chem.*, 1915, **21**, 345—350).—In view of the isolation of a diazo-ester having the constitution



by the action of nitrous acid on ethyl benzylideneglucosamate, the authors are of the opinion that the replacement of the amino-group by hydroxyl and halogen in amino-acids and esters takes place owing to the intermediate formation of diazo-compounds of this type, and explain the formation of epimeric or stereoisomeric derivatives from the free amino-acids and their esters respectively on the assumption that the production of the diazo-compound is followed by another intermediate phase in which one of the nitrogen atoms becomes detached from the carbon atom, whilst the other still remains united to it, the nitrogen atom to become detached first being determined by the nature of the other groups in combination with the original asymmetric carbon atom. The difference in the behaviour of the free amino-acid and ester may be represented by the following scheme:



Whether the above views apply to the simpler amino-acids, in which the formation of a diazo-compound is accompanied by the complete loss of molecular asymmetry, or only to the hexosamic acids where the

formation of a diazo-compound at the α-carbon atom does not involve the complete disappearance of the asymmetric character of the remainder of the molecule, is not definitely stated.

Ethyl monobenzylideneglucosamate hydrochloride, $C_{15}H_{22}O_6NCl$, prepared by passing hydrogen chloride into a suspension of glucosamic acid in a solution of benzaldehyde in alcohol, forms long, colourless needles, m. p. 167—168° (decomp.), and, on treatment with sodium nitrite and acetic acid in aqueous solution at 0°, is converted into *ethyl diazobenzylideneglucosamate* [*βγ-dihydroxy-δε-benzylidenedioxy-α-diazohexoate*] (formula I above), which forms a light yellow powder, and reacts with ethereal hydrogen chloride and hydrogen bromide with evolution of nitrogen, but neither of the resulting compounds nor the products formed from them by the removal of the benzylidene residue have yet been isolated in a state of purity. F. B.

Hydrazides and Azoimides of Organic Acids. XXXI. Hydrazides and Azoimides of Oxalic Acid. THEODOR CURTIUS [and KARL HOCHSCHWENDER] (*J. pr. Chem.*, 1915, [ii], **91**, 415—441. Compare this vol., i, 124, 169).—This paper deals mainly with the preparation and reaction of the hydrazide and azoimide of oxamic acid and the semihydrazide, $NH_2{\cdot}NH{\cdot}CO{\cdot}CO_2Et$, and semiazoimide, $N_3{\cdot}CO{\cdot}CO_2Et$, of ethyl oxalate.

When heated with acetic anhydride, oxamylhydrazide (semioxamazide) (Kerp and Unger, A., 1897, i, 270) yields a *diacetyl* derivative, $NH_2{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}NAc_2$, crystallising in lustrous, white, silky needles, m. p. 184—185°; the *benzoyl* derivative, $NH_2{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}NHBz$, prepared from the hydrazide and benzoyl chloride in the presence of aqueous sodium carbonate, forms clusters of slender, white needles, m. p. 231—232°.

On treatment with sodium nitrite at −5° in aqueous solution, oxamylhydrazide hydrochloride is converted into *oxamylazoimide*, $NH_2{\cdot}CO{\cdot}CO{\cdot}N_3$, which crystallises in microscopic needles or plates, and explodes when rubbed or heated at 115°. When warmed with alcohol, the azoimide is transformed into ethyl allophanate; with water it yields azoimide, oxamic acid, and a substance, m. p. 117°; with moist acetone it gives rise to carbamide.

At the ordinary temperature, it reacts with aniline and *p*-toluidine in acetone solution and with phenylhydrazine in ethereal solution, yielding *as*-phenylbiuret, *as*-*p*-tolylbiuret (Pickard and Carter, T., 1900, **79**, 844), and oxamylphenylhydrazide respectively.

In addition to the azoimide described above, the action of sodium nitrite on oxamylhydrazide hydrochloride gives rise to *hydrazidioxamide* (s-*dioxamylhydrazide*), $N_2H_2(CO{\cdot}CO{\cdot}NH_2)_2$, which separates from water in white flocks, m. p. 302—303° (decomp.). That the last-named substance owes its formation to the interaction of oxamylazoimide with unaltered oxamylhydrazide is shown by the fact that it is the sole product when only half the theoretical amount of nitrite necessary for the conversion of the hydrazide into the azoimide is employed. Hydrazidioxamide possesses marked acid properties and yields a yellow *silver* salt.

Ethyl oxalhydrazinate, $NH_2{\cdot}NH{\cdot}CO{\cdot}CO_2Et$, obtained together with

a small amount of oxalhydrazide by the interaction of ethyl oxalate and hydrazine hydrate below −13°, crystallises in short, stout needles, m. p. 52—53°, evolves gas and solidifies at 152°, and then remains unfused even at 300°. It decomposes slowly when kept, and reacts with concentrated aqueous ammonia and with benzaldehyde to form oxamylhydrazide and the benzylidene derivative, m. p. 133—134°, described by Stollé (A., 1911, i, 357); the condensation product with acetone forms a syrup. On treatment with ethereal hydrogen chloride, its alcoholic solution yields a *hydrochloride* which crystallises in deliquescent, lustrous, white leaflets, m. p. 107—108°, and reacts with sodium nitrite at a low temperature to form the *semiazoimide* of ethyl oxalate (*ethyl oxalazoimate*), $CO_2Et{\cdot}CO{\cdot}N_3$. The latter substance forms a colourless oil, and when boiled in alcoholic solution is converted into ethyl iminodicarboxylate (Diels, A., 1903, i, 324). It is accompanied by *ethyl hydrazidioxalate*, $N_2H_2(CO{\cdot}CO_2Et)_2$, which crystallises in slender, white, doubly-refractive needles, m. p. 125—126°, and may also be prepared (1) by oxidising ethyl oxalhydrazinate with mercuric oxide in alcoholic solution, and (2) by heating a mixture of ethyl oxalate and ethyl hydrazinate at 130—140°. Ethyl hydrazidioxalate acts as a monobasic acid, forms a stable, white *silver* salt, and a yellowish-white *barium* salt. On treatment with aqueous ammonia, it is converted into the hydrazidioxamide described above. It is hydrolysed by aqueous sodium hydroxide to the free *acid*, $N_2H_2(CO{\cdot}CO_2H)_2$, m. p. 174—175°, which crystallises with $3H_2O$ in colourless plates, m. p. 126°, and forms sparingly soluble, white *silver* and *lead*, green *cupric* and white, gelatinous *calcium* salts.

With hydrazine hydrate in alcoholic solution, it yields *hydrazioxaldihydrazide*, $N_2H_2(CO{\cdot}CO{\cdot}NH{\cdot}NH_2)_2$. This crystallises in long, colourless, thin needles, m. p. above 300°, forms a *hydrochloride*, B,2HCl, a crystalline *nitrate* and a *dibenzylidene* derivative,

$$N_2H_2(CO{\cdot}CO{\cdot}NH{\cdot}N{:}CHPh)_2,$$

as a white, microcrystalline powder, m. p. above 300°.

Hydrazidioxalazoimide, $N_2H_2(CO{\cdot}CO{\cdot}N_3)_2$, prepared from the preceding dihydrazide and sodium nitrite in hydrochloric acid solution, forms an explosive white powder, and is converted by boiling with alcohol into the *urethane*, $N_2H_2(CO{\cdot}NH{\cdot}CO_2Et)_2$, colourless, rhombic leaflets or rectangular pyramids, m. p. 200·5°, the constitution of which has been established by its hydrolysis with dilute sulphuric acid into ammonia, carbon dioxide, alcohol and hydrazine.

The preparation of the normal and acid hydrazine salts of oxalic acid are also described (compare Turrentine, A., 1910, i, 388).

F. B.

Researches on Silicon Compounds. IX. Action of Alkalis and Water on Hexaethoxysilicoethane, Silico-oxalic Acid, Mesosilico-oxalic Acid, and Chloropentaethoxysilicoethane, Together with Some Remarks on their Constitution. Geoffrey Martin (T., 1915, **107**, 1043—1050).—Hexaethoxysilicoethane evolved hydrogen on treatment with potassium hydroxide corresponding in amount to one molecule for every Si–Si linking, and this is held to confirm the author's theory that when hydrogen is

evolved from organic silicon compounds by treatment with alkali it corresponds to the conversion of a :Si–Si: into a :Si–O–Si: group. The action of ammonia on silico- and mesosilico-oxalic acids gave rise to unstable silicic acids which on drying in a vacuum over sulphuric acid lost all their water and left physically and chemically identical specimens of silica. The evolution of hydrogen in the above reactions corresponds with the conversion of three Si·Si linkings into Si·O·Si, and constitutional formulæ are suggested for each of the substances concerned, for which the original paper must be consulted. An attempt was made to replace chlorine by hydroxyl in the chloroethoxysilicoethanes, so as to study the tendency of the hydroxy-products to lose water, but the action of water on chloropentaethoxysilicoethane did not take the expected course, complex condensation products and ethyl alcohol being mainly produced. G. F. M.

Unsaturated Hydroaromatic Hydrocarbons. K. VON AUWERS and W. TREPPMANN (*Ber.*, 1915, **48**, 1207—1225).—In an investigation of the dehydration product of 1-benzyl*cyclo*hexan-1-ol (Sabatier and Mailhe, A., 1904, i, 666), Klages and Friedemann (*Diss.*, Heidelberg, 1907) came to the conclusion that the constitution of this substance was that of 1-benzyl-Δ^1-*cyclo*hexene, and not of benzylidene*cyclo*hexane, but further confirmation of this point seemed desirable.

It would be expected that dehydration of phenyl*cyclo*hexylcarbinol should yield benzylidene*cyclo*hexane, but the product is identical with that derived from 1-benzyl*cyclo*hexan-1-ol, so that intramolecular change must occur in one of these processes; the specific refraction of the product, however, definitely favours the idea that the substance has not the structure of benzylidene*cyclo*hexane which includes a conjugated double linking.

Chemical evidence is also available as to this point. The nitrosochloride of benzylidene*cyclo*hexane should be convertible into benzoyl-*cyclo*hexane, whilst that of the benzyl*cyclo*hexene under analogous treatment should pass through the stages:

$$CH_2Ph\cdot C\lessdot\begin{matrix}CH_2\cdot CH_2\\CH{-}CH_2\end{matrix}\gtrdot CH_2 \longrightarrow CH_2Ph\cdot CCl\lessdot\begin{matrix}CH_2\text{———}CH_2\\C(:NOH)\cdot CH_2\end{matrix}\gtrdot CH_2$$

$$\longrightarrow CH_2Ph\cdot C\lessdot\begin{matrix}CH\text{———}CH_2\\C(:NOH)\cdot CH_2\end{matrix}\gtrdot CH_2 \longrightarrow CH_2Ph\cdot C\lessdot\begin{matrix}CH\cdot CH_2\\CO{-}CH_2\end{matrix}\gtrdot CH_2$$

$\longrightarrow CH_2Ph\cdot C_6H_9O$, the final product being 2-benzyl*cyclo*hexanone. The product of this series of changes was not benzoyl*cyclo*hexane, and was therefore presumably 2-benzyl*cyclo*hexanone, thus confirming the identity of the original hydrocarbon as a benzyl*cyclo*hexene.

1-Benzyl-Δ^1-*cyclo*hexene gave a colourless *nitrosochloride*, m. p. 106—110°; when heated with sodium acetate in acetic acid containing a little sulphuric acid, the nitrosochloride was converted into the *oxime*, needles, m. p. 136—138°, which, on hydrolysis with dilute sulphuric acid, yielded 1-*benzyl*-Δ^1-cyclo*hexen*-2-*one*, a colourless oil, b. p. 174°/16 mm., D_4^{20} 1·063, n_D^{20} 1·5635; *semicarbazone*, needles, m. p. 157—161°. Reduction of the unsaturated ketone with hydrogen and colloidal palladium produced 1-benzyl*cyclo*hexan-2-one, an oil; *semicarb-*

azone, needles, m. p. 166—167°, distinct from that of benzoyl*cyclo*hexane, m. p. 168—169°.

The authors confirm the results of Klages (A., 1907, i, 499), who found that diethylenic compounds, such as 5-phenyl-1 : 3-dimethyl-$\Delta^{3:5}$-*cyclo*hexadiene, are characterised by high refractive and dispersive power, although on account of the sensitiveness of these compounds to chemical change it is difficult to obtain quite concordant values.

D. F. T.

A By-product of the Manufacture of Trinitrotoluene. E. MOLINARI and M. GIUA (*Chem. Zentr.*, 1914, ii, 762; from *Zeitsch. ges. Schiess- Sprengstoff-wesen.*, 1914, **9**, 239—242).—In the oily substance obtained by centrifuging the crude solid dinitrotoluene, the following compounds were identified: 3- and 4-nitrotoluenes, 2 : 4-, 2 : 5-, 2 : 6- and 3 : 4-dinitrotoluenes, 2 : 4 : 6-trinitrotoluene, and a new *trinitrotoluene* melting at 79·5°, nitro-groups in which occupy the positions 2 : 3 : 5 or 2 : 3 : 6. Other products also seem to be present and are under investigation.

G. F. M.

The Fifth (ε-) Trinitrotoluene and the Corresponding Halogenated Dinitro-products. W. KÖRNER and A. CONTARDI (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 888—896. Compare A., 1914, i, 263, 509).—As well as by the action of alcoholic ammonia on the methyl or ethyl ether of 3 : 5-dinitro-*o*-cresol, 3 : 5-dinitro-*o*-toluidine may be obtained in the following manner. Treatment of aceto-*o*-toluidide with a mixture of nitric and acetic acids yields a mixture of 3- and 5-nitroaceto-*o*-toluidides. These may be separated either by partial hydrolysis with alcoholic potassium hydroxide, which converts the 5-derivative into 5-nitro-*o*-toluidine and leaves the 3-derivative unchanged, or by fractional crystallisation from alcohol. Treatment of either 3- or 5-nitroaceto-*o*-toluidide or of a mixture of them with nitric acid (D 1·52) at 0° yields 3 : 5-dinitroaceto-*o*-toluidide, which is converted by the action of concentrated sulphuric acid into 3 : 5-dinitro-*o*-toluidine. From the latter, 2 : 3 : 5-trinitrotoluene is obtained by the method previously described (*loc. cit.*).

3-Nitroaceto-*o*-toluidide, $NO_2 \cdot C_6H_3Me \cdot NHAc$, forms large, shining prisms or plates, m. p. 158° (compare Lellmann and Würthner, A., 1885, 974), and the isomeric 5-nitro-compound, short, white needles, m. p. 201·6°.

3 : 5-*Dinitroaceto-o-toluidide*, $NHAc \cdot C_6H_2Me(NO_2)_2$, forms slender, white needles, m. p. 205·2°.

2 : 3 : 5-*Trinitrotoluene*, $C_6H_2Me(NO_2)_3$, forms large, slightly yellow prisms, m. p. 97·2°. [ARTINI. The crystals belong to the bipyramidal class of the rhombic system; $a : b : c = 0{\cdot}6393 : 1 : 0{\cdot}3725$, and those of 3 : 4 : 5-trinitrotoluene to the prismatic class of the monoclinic system; $a : b : c = 1{\cdot}4275 : 1 : 0{\cdot}9176$, $\beta = 58°36'$.] In acetone containing a few drops of ammonia solution it dissolves, giving a rose-red coloration, which changes to red, then to brown and finally to black; it reacts extremely readily with alkalis.

2 : 3 : 5-*Trinitrobenzoic acid*, $C_6H_2(NO_2)_3 \cdot CO_2H$, prepared by oxidising 2 : 3 : 5-trinitrotoluene with chromic acid, forms shining, rhombic

plates, m. p. 82° ($+2H_2O$) or 171° (anhydrous), and is converted into 3 : 5-dinitrosalicylic acid when boiled with water.

3 : 5-*Dinitro*-2-*methoxybenzoic acid*, $OMe{\cdot}C_6H_2(NO_2)_2{\cdot}CO_2H$, obtained by heating 2 : 3 : 5-trinitrobenzoic acid with absolute methyl alcohol in a sealed tube at 125°, forms shining, tabular crystals, m. p. 132°.

2-*Chloro*-3 : 5-*dinitrotoluene*, $C_6H_2MeCl(NO_2)_2$, obtained by treating an aqueous solution of 3 : 5-dinitrotoluene-2-diazonium nitrate with cupric chloride in presence of ice, forms large prisms, m. p. 65°.

2-*Bromo*-3 : 5-*dinitrotoluene*, $C_6H_2MeBr(NO_2)_2$, obtained similarly by means of cupric bromide, forms large, pale yellow prisms, m. p. 95°.

2-*Iodo*-3 : 5-*dinitrotoluene*, $C_6H_2MeI(NO_2)_2$, prepared in an analogous manner, forms groups of small, lemon-yellow plates or long prisms, m. p. 119·5°. T. H. P.

Studies in Orientation. Nitration Products of 3-Chloro-5-bromotoluene. Julius Behrend Cohen and Wallace Jennings Murray (T., 1915, **107**, 847—851).—In order to determine the relative orienting effect of the electropositive methyl group and that of the chlorine and bromine atoms, the authors have investigated the nitration of 3-chloro-5-bromotoluene, and find that the first nitro-group replaces the hydrogen between the methyl and bromine atom, whilst the second nitro-group probably enters the ring between the methyl and chlorine atom. These results are in agreement with the observations of Cohen and Dakin (T., 1902, **81**, 1344) on the nitration of the dichlorotoluenes, namely, that where the nitro-group cannot avoid entering the nucleus between two other groups, it selects the position between the methyl group and a halogen in preference to that between two halogen atoms.

3-Chloro-5-bromotoluene, m. p. 25°, has been prepared from aceto-*p*-toluidide (1) by successive bromination and chlorination with hydrochloric acid and sodium chlorate in acetic acid solution, followed by hydrolysis to 3-chloro-5-bromo-4-toluidine, m. p. 63·5°, and elimination of the amino-group by means of the diazo-reaction; (2) by chlorination and hydrolysis to 3-chloro-4-toluidine, b. p. 110°/10 mm., and subsequent bromination and removal of the amino-group. Although the two halogens were thus introduced in a different order, the products proved to be identical.

The *diacetyl* derivative of 3-chloro-5-bromo-4-toluidine has m. p. 82°, and is hydrolysed to the *monoacetyl* derivative, m. p. 199°.

On nitration with fuming nitric acid below 5°, 3-chloro-5-bromotoluene yields 3-chloro-5-bromo-6-nitrotoluene, colourless needles, m. p. 71°, which is reduced by tin and hydrochloric acid to 3-*chloro*-5-*bromo* 6-*toluidine*, m. p. 42°. The position of the nitro-group has been established by the formation of the last-named substance from aceto-*o*-toluidide by successive chlorination, hydrolysis, and bromination. When heated with acetic anhydride, 3-chloro-5-bromo-6-toluidine yields a *diacetyl* derivative, colourless needles, m. p. 85°, which is hydrolysed by aqueous sodium hydroxide to the *monoacetyl* derivative, colourless needles, m. p. 187°.

3-*Chloro*-5-*bromo*-2-*toluidine*, prepared by brominating aceto-*o*-toluidide, followed by chlorination and hydrolysis, forms colourless

needles, m. p. 60°, and yields a *monoacetyl* derivative, m. p. 171°; *diacetyl* derivative, m. p. 90·5°. The position of the halogens has been determined by the formation of 3-chloro-5-bromotoluene on eliminating the amino-group by diazotisation.

On further nitration, 3-chloro-5-bromo-6-nitrotoluene yields a dinitro-derivative, colourless prisms having a brilliant lustre, m. p. 144° (compare Cohen and Smithells, T., 1914, **105**, 1907), and a *trinitro*-derivative, m. p. 211°, from which the halogens are readily removed by alkali hydroxides.

The high m. p. of the dinitro-derivative points to a symmetrical structure, so that the second nitro-group is probably in position 2.

F. B.

α-Arylsulphonylpropionitriles. J. Troeger and Wunderlich (*Arch. Pharm.*, 1915, **253**, 214—232. Compare A., 1905–1908).—It has been shown that α-arylsulphonacetonitriles form salts when they dissolve in cold alkali hydroxides, from which α-dialkyl derivatives, $RSO_2 \cdot CR_2 \cdot CN$, but not mono-alkyl compounds, could be prepared (A., 1905, i, 870). Some mono-methyl compounds have now been obtained in the original way, namely, by the action of the sodium arylsulphinates on α-chloropropionitrile, details for the preparation of which, by Henry's method (A., 1899, i, 183), are given. The reaction is more difficult of achievement in the propionic series.

Henry found (*ibid.*) that many acetonitrile derivatives had the same b. p. as the corresponding propionitriles, but the present arylsulphonpropionitriles have much lower m. p.'s than the non-methylated ones.

Sodium benzenesulphinate and α-chloropropionitrile, moistened with alcohol, were heated at 130—140° for eight hours in a sealed tube, and the *α-benzenesulphonylpropionitrile*, $SO_2Ph \cdot CHMe \cdot CN$, was obtained in prismatic needles, m. p. 72°. Unlike α-benzenesulphonylacetonitrile, the compound is insoluble in sodium hydroxide. It was originally thought that the soluble nitriles were difficultly hydrolysable, but both of these compounds are hydrolysed to the corresponding fatty acids to the maximum extent of about 68% when warmed with 0·1*N*-sodium hydroxide for three hours. Longer heating causes the scission of the salts of these acids into sulphones, thus:

$$SO_2Ph \cdot CHMe \cdot CO_2Na + H_2O = SO_2PhEt + NaOH + CO_2.$$

α-Benzenesulphonylpropionamide was obtained after warming the nitrile with 0·1*N*-sodium hydroxide until it dissolved, in stout needles, m. p. 150°.

When heated with alcoholic hydroxylamine for three hours, the nitrile condensed to *β-benzenesulphonylpropenylamidoxime*,

$$SO_2Ph \cdot CHMe \cdot C(NH_2):N \cdot OH,$$

prismatic needles, m. p. 147°, but, after six hours, the product was a *compound*, $C_9H_{10}O_2N_2S$, m. p. 79°, differing from the former by H_2O. The nitrile also reacted readily with alcoholic ammonium sulphide, yielding *α-benzenesulphonylthiopropionamide*, m. p. 159°.

α-p-Toluenesulphonylpropionitrile was obtained in stellar granules, m. p. 66°, converted into *α-p-toluenesulphonylpropionamide*, scales, m. p. 166°, the *thioamide*, $C_7H_7SO_2 \cdot CHMe \cdot CS \cdot NH_2$, pale yellow,

prismatic needles, m. p. 149°, and into *β*-p-*toluenesulphonylpropenylamidoxime*, m. p. 140—141°.

α-p-*Chlorobenzenesulphonylpropionitrile*, rhombic scales, m. p. 101—102°, gave the corresponding *amide*, m. p. 190°, *thioamide*, m. p. 140—141°, and *amidoxime*, m. p. 141°. *α*-p-*Bromobenzenesulphonylpropionitrile*, scales, m. p. 98°, yielded the *amide*, m. p. 196·5°, the *thioamide*, m. p. 176°, and the *amidoxime*, with $\frac{1}{2}H_2O$, stellar aggregates of prismatic needles, m. p. 145°. *α*-p-*Iodobenzenesulphonylpropionitrile*, prismatic needles, m. p. 115°, was converted into the *amide*, m. p. 210°, *thioamide*, m. p. 182°, and the *amidoxime*, stellar needles, m. p. 167°. J. C. W.

Preparation of *o*-Chlorotoluene-*p*-sulphonic Acid. Farbwerke vorm. Meister, Lucius & Brüning (Fr. Pat. 473518; from *J. Soc. Chem. Ind.*, 1915, **34**, 708).—*o*-Chlorotoluene-*p*-sulphonates separate out immediately when concentrated aqueous solutions of toluene-*p*-sulphonates are treated with chlorine at temperatures below 70—80°. If the toluene-*p*-sulphonates contain toluene-*o*-sulphonate, the latter is converted into a chloro-derivative which remains in solution. G. F. M.

Acenaphthylene and its Derivatives. Bertram Campbell (T., 1915, **107**, 918—921).—*Acenaphthylene* was prepared by passing the vapour of acenaphthene through a hot silica tube, and formed square, yellow plates, m. p. 93°. By the action of chlorine in carbon tetrachloride solution it was converted into 1 : 2-*dichloroacenaphthene*, $C_{10}H_6<\begin{matrix}CHCl\\|\\CHCl\end{matrix}$, white plates, m. p. 115°, which on oxidation with permanganate gave naphthalic acid, and on treatment with alcoholic sodium ethoxide lost hydrogen chloride with the formation of 1-*chloroacenaphthylene*, a yellow oil. Iodine causes polymerisation of acenaphthylene to a yellow powder, probably identical with the polyacenaphthylene of Dziewonski and Leyko (A., 1914, i, 825). G. F. M.

Reaction Differences of Stereoisomeric Ethylene Haloids. II. P. Pfeiffer [with K. von Swidzinski] (*Ber.*, 1915, **48**, 1048—1058. Compare A., 1912, i, 618).—In the earlier communication attention has been drawn to the marked difference in the behaviour of the stereoisomeric dibromides derived from stilbene and 2 : 4-dinitrostilbene towards treatment with pyridine; the less fusible stereoisomeride in each case eliminated bromine, regenerating the parent compound, whilst the more fusible yielded hydrogen bromide in each case with formation of an *α*-bromostilbene derivative.

In extension of this investigation other compounds of a similar character have been examined. Of the stereoisomeric dibromides derived from 2-nitrostilbene, the less fusible *α*-compound (pale yellow tablets, m. p. 156°) yielded almost entirely 2-nitrostilbene, whilst the more fusible *β*-isomeride (prisms, m. p. 89°) produced *α*-bromo-2-nitrostilbene, $NO_2\cdot C_6H_4\cdot CBr{:}CHPh$, the treatment with pyridine being performed at water-bath temperature. In the case of the stereoisomeric dibromides derived from cinnamic acid the observed difference

was less marked, for whereas the more fusible $\alpha\beta$-dibromophenylpropionic acid (m. p. 83—91°) passed almost quantitatively into α-bromocinnamic acid, the less fusible stereoisomeride (m. p. 195°) underwent concurrent elimination of bromine and hydrogen bromide, yielding a mixture of cinnamic acid and α-bromocinnamic acid in the approximate ratio of 62:38. The behaviour of the corresponding stereoisomeric forms of methyl $\alpha\beta$-dibromophenylpropionate was analogous to the last case, the compound, m. p. 50—52°, eliminating hydrogen bromide, whilst the isomeride, m. p. 117°, suffered concurrent scission of bromine and hydrogen bromide.

This characteristic difference seems to be limited to the stereoisomeric dibromides derived from aromatic ethylene derivatives, and it was found that the action of pyridine on the two dibromides of crotonic acid (that is, on the two forms of $\alpha\beta$-dibromobutyric acid) gave in each case only α-bromocrotonic acid as product (compare Pfeiffer and Langenberg, A., 1910, i, 810); in a similar manner the dibromides of maleic and fumaric acids (the isomeric dibromosuccinic acids) both yielded hydrogen bromide on treatment with pyridine, although the process is in this case complicated by the subsequent entry of pyridine into the molecule of the product (compare Pfeiffer, Langenberg, and Birencweig, A., 1910, i, 878). D. F. T.

Preparation of Polychloroanthracenes. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 282818; from *J. Soc. Chem. Ind.*, 1915, **34**, 710).—Treatment of the chlorine additive products of 9 : 10-dichloroanthracene with aqueous alkali in presence of alkali salts of benzylsulphanilic acid results in the formation of polychloroanthracenes, the reaction commencing at ordinary temperatures, and rapidly becoming complete on warming. Thus, for example, dichloroanthracene tetrachloride gives an almost theoretical yield of 1 : 3 : 9 : 10-tetrachloroanthracene, the hexachloride gives a pentachloroanthracene, and the octachloride a hexachloroanthracene. These yellow polychloroanthracenes are used in pigment colours, and as intermediate products in the preparation of chlorinated anthraquinones and dyes. G. F. M.

Preparation of Sulphonyl Chlorides of the Anthracene Series. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 281911; from *J. Soc. Chem. Ind.*, 1915, **34**, 708).—The action of chlorosulphonic acid on anthraquinone or β-chloroanthraquinone results in the formation of the chlorides of dichloroanthracenedisulphonic acids. G. F. M.

A New Dibromophenanthrene. Bromination of Phenanthrene in Acetic Acid. HÅKAN SANDQVIST (*Ber.*, 1915, **48**, 1146—1149).—When kept for several months, the mother liquors from the preparation of 10-bromophenanthrene by the action of bromine on phenanthrene in acetic acid solution, deposited a small quantity of a new *dibromophenanthrene*, colourless needles, m. p. 123°, a lower m. p. being observed if the re-solidified fusion is placed in a bath at 110—120°; fusion with potassium hydroxide at 250° yielded a bromine-free phenolic *substance*, and reduction with alcoholic ammonia

and zinc dust converted the dibromo-compound into phenanthrene. When oxidised with chromic anhydride in acetic acid solution, the dibromo-compound passes into a *monobromophenanthraquinone*, golden-yellow needles, m. p. 233—234° (*oxime*, golden leaflets, m. p. 213° with decomp.), which is quite distinct from the bromophenanthraquinone of Schmidt (A., 1904, i, 1033). The disappearance of one bromine atom during the oxidation indicates its location in the 9 or 10 position, and the remaining bromine atom must be in position 1 or 4, because 2- and 3-bromophenanthraquinones are already known. In the new dibromophenanthraquinone therefore, if position 10 is assumed for the one bromine atom, the other must be in one of the positions 1, 4, 5 or 8. D. F. T.

A Highly Viscous Aqueous Solution of Two Acids, which is Sensitive to Light. HÅKAN SANDQVIST. (*Arkiv Kem. Min. Geol.*, 1914, **5**, No. 17, 1—61).—In a previous communication (A., 1913, i, 846) the author has pointed out that an aqueous solution of 10-bromophenanthrene-3- or -6-sulphonic acid is very little more viscous than water, but the addition of a strong mineral acid makes it highly viscous. In a detailed series of measurements the author now shows that: (1) the viscosity increases very strongly with the concentration of the sulphonic acid or mineral acid (hydrochloric acid); (2) the temperature-coefficient of viscosity is much greater than with solutions of crystalloids; (3) the electrical conductivity is independent of the viscosity; (4) the solution is optically non-homogeneous. Exposure to light diminishes the viscosity, but the reaction is not reversed again on keeping in the dark. If the sulphonyl chloride or ester is then formed and the acid regenerated, the viscous properties are once more obtained; regeneration by means of the barium salt does not, however, alter the viscosity.

Experiments with sulphuric, acetic, monochloroacetic, and nitrotoluenesulphonic acids showed that the increase in viscosity depended mainly on the concentration of the hydrion. Acetic and monochloroacetic acids have no effect, owing to their slight dissociation. Nitrotoluenesulphonic acid also has no effect, although at the concentration used it probably has the same hydrion concentration as sulphuric acid. Freezing-point measurements indicated that increase in viscosity is accompanied by an increase in molecular weight.

The author explains his results on the assumption that 10-bromophenanthrene-3- or -6-sulphonic acid exists in two forms, the *a* and *b* forms.

These forms are not identical with the "unilluminated" and "illuminated" acids respectively, but form the chief constituents of these acids. The *a*-form results by decomposition of the sulphonyl chloride, or ester, with water at high temperatures; the *b*-form is produced by illumination of the *a*-form, but the change is not complete. Change from the *b*- to the *a*-form does not take place in the dark, and can only be brought about by the preparation of the chloride, or ester, and its decomposition with water. Each form gives a series of salts having different solubilities, water of crystallisation, etc. The most striking property of the *a*-form is the formation of highly viscous

systems under the influence of hydrions; illumination changes the *a*-into the *b*-form, the viscosity then decreasing.

In solution, the *a*-form shows the properties of a substance which is intermediate between a crystalloid and a colloid. In many respects its behaviour is similar to that of a lyophile colloid. T. S. P.

Triphenylmethyl. HEINRICH WIELAND (*Ber.*, 1915, **48**, 1096—1097).—The preparation of triphenylmethyl is greatly facilitated by using light petroleum as solvent in place of benzene in the usual process (Schmidlin, A., 1908, i, 150; Schlenk, Weickel and Herzenstein, A., 1910, i, 236); hexaphenylethane is much less soluble in light petroleum, and can be made to crystallise out by cooling the solution. Full experimental details are given.

On account of the gradual re-adjustment of equilibrium when a benzene solution of triphenylmethyl is diluted, it is possible by using a glass cylinder to demonstrate successively Beer's law and Piccard's colorimetric dilution law (A., 1911, ii, 561). The influence of the solvent on the extent of the dissociation of hexaphenylethane also can be shown by diluting two benzene solutions of the same concentration, one with benzene and the other with light petroleum. D. F. T.

Preparation of Aromatic Amines. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 282492; from *J. Soc. Chem. Ind.*, 1915, **34**, 652).—Nitro-compounds are volatilised with steam and the mixture passed with hydrogen over catalysts heated to a temperature below the boiling point of the nitro-compound. Thus a mixture of steam and hydrogen is passed into nitrobenzene heated at 120°, and the vapours are led over finely divided nickel. The yield of aniline is almost theoretical. G. F. M.

Preparation of Aromatic Amines from Nitro-compounds. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 282568; from *J. Soc. Chem. Ind.*, 1915, **34**, 708).—Nitro-compounds are reduced by hydrogen, or gases containing hydrogen, in presence of metallic copper and of activators. The copper is prepared by ignition, or by reduction with hydrogen or carbon monoxide at low temperatures of a salt, suitable salts being those which give indifferent gases on heating, such as the carbonate, formate, oxalate or nitrate, or mixtures of copper salts with ammonium carbonate. If copper formate is used, the reduction temperature may be below 300°. The copper may be used as such, or on pumice, asbestos, etc., with the addition of alkali compounds or metallic oxides, such as magnesia or alumina, as activators. The reaction is carried out at temperatures below 200°, otherwise impure products are produced and the activity of the catalyst decreases. G. F. M.

Action of Methyl Ethyl Ketone on 2 : 3 : 4 : 6-Tetranitrophenylmethylnitroamine. P. VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 98—100).—The decomposition of 2 : 3 : 4 : 6-tetranitrophenylmethylnitroamine by hot water (Romburgh, A., 1889, 1154) can be effected more conveniently with moist acetone and even still more satisfactorily with moist methyl ethyl ketone. A

solution in the last solvent at the ordinary temperature gradually gives a crystalline deposit of 2 : 4 : 6-trinitromethylnitroaminophenol, the supernatant liquid subsequently being found to contain hydrocyanic acid, diacetyl, and α-oximino-methyl-ethyl-ketone. The presence of moisture appears to be necessary to this reaction, the nitrous acid formed by hydrolysis at an early stage in the change being largely responsible for the formation of the above products.

D. F. T.

Formation of Chlorinated Amines by the Reduction of Nitro-compounds. Winifred Grace Hurst and Jocelyn Field Thorpe (T., 1915, **107**, 934—941).—3-*Chloro*-p-*phenetidine* was obtained in 90% yield by the reduction of *p*-nitrophenetole with tin and concentrated hydrochloric acid, whilst the reaction proceeded normally with production of *p*-phenetidine when dilute hydrochloric acid was used. The chlorinated amine was separated from traces of the unchlorinated product by extracting the aqueous solution of its acetate with ether. It forms a colourless liquid, b. p. 161·5°/33 mm. When cooled in ice it solidifies to colourless needles, m. p. 24°. On acetylation with acetic anhydride, it gives 3-*chloroaceto*-p-*phenetidide*, m. p. 97°. The compound described under this name by Orton and King (T., 1911, **99**, 1190) is correctly the 2-chloro-compound. 3-Chloroaceto-*p*-phenetidide when treated with aluminium chloride in benzene solution is hydrolysed to 3-*chloro*-4-*acetylaminophenol*, which forms long prisms, m. p. 121°. Corresponding derivatives of anisidine were also prepared. 3-*Chloro*-p-*anisidine* is a feeble base, boiling at 156°/31 mm. Its *acetyl* derivative melts at 114°.

3-Chloro-*p*-phenetidine forms a brilliant red azo-compound, 2-*chloro*-4-*ethoxybenzeneazo*-β-*naphthol*, with β-naphthol. With acetoacetic ester it reacts to form s-*di*-2-*chloro*-4-*ethoxyphenylcarbamide*,

$$OEt\cdot C_6H_3Cl\cdot NH\cdot CO\cdot NH\cdot C_6H_3Cl\cdot OEt,$$

slender needles, m. p. 235°, b. p. 287°. The corresponding s-*di*-2-*chloro*-4-*hydroxyphenylcarbamide* is produced by hydrolysis of the above with aluminium chloride. It melts at 251°, and forms a *diacetyl* derivative, m. p. 227°. s-*Di*-3-*chloro*-4-*ethoxyphenylcarbamide* was obtained by the action of acetoacetic ester on 2-chloro-*p*-phenetidine. It forms slender needles, m. p. 211°.

G. F. M.

The Grignard Reaction with Nitroso-compounds. Heinrich Wieland and Alexander Roseeu (*Ber.*, 1915, **48**, 1117—1121).—The nitroso-group in many reactions exhibits similar behaviour to the carbonyl group, so that a reaction might be expected with organomagnesium compounds according to the scheme $R\cdot N{:}O + BrMgR' \longrightarrow NRR'\cdot OMgBr \longrightarrow NRR'\cdot OH$, but the change generally goes further, the hydroxylamine derivative undergoing reduction, so that the final product is a secondary amine, the subsequent course of the change being presumably $NRR'\cdot OMgBr + BrMgR' \longrightarrow$

$$NRR'\cdot MgBr + MgBr\cdot OR' \longrightarrow NHRR' + R'\cdot OH.$$

In the case of nitrosobenzene, both diphenylhydroxylamine and diphenylamine can be obtained (Wieland and Roseeu, A., 1912, i, 253), and by the action of magnesium *p*-tolyl bromide on *p*-nitrosotoluene in ethereal solution, *di*-p-*tolylhydroxylamine*, m. p. 91—92°

(decomp.), has been obtained; this decomposes under the influence of mineral acids, giving, amongst other compounds, *ditolyldihydrotolazine*, $C_6H_3Me\langle^{N(C_6H_4Me)}_{N(C_6H_4Me)}\rangle C_6H_3Me$, and is also reducible to di-*p*-tolylamine.

The action of the Grignard reagent on nitrosoamines in the aliphatic group (Wieland and Fressel, A., 1911, i, 495) is more complicated than with aromatic compounds, the interaction of magnesium phenyl bromide and diphenylnitrosoamine yielding triphenylhydrazine together with a little diphenylamine, probably produced by fission of the former compound. This fission of the hydrazine product occurs the more easily the weaker the attachment of the ·NO group, and with nitrosocarbazole and nitrosoacetanilide, magnesium phenyl bromide gives good yields of diphenylamine.

Copper powder does not effect the usual type of reaction between aryl haloids and phenylhydroxylamine with production of a diarylhydroxylamine; the interaction of *o*-iodobenzoic acid and phenylhydroxylamine yields azoxybenzene and phenylanthranilic acid, leaflets, m. p. 181°. D. F. T.

The *p*-Anisidide and *p*-Phenetidide of α-Thiolacetic Acid. H. Beckurts and G. Frerichs (*Arch. Pharm.*, 1915, **253**, 136—155. Compare the anilide, A., 1902, i, 763; 1906, i, 650).—*p*-Anisidine, chloroacetic acid, and potassium thiocyanate were boiled together in alcoholic solution until potassium chloride separated, when *α-carbamylthiolaceto*-p-*anisidide*, $NH_2{\cdot}CO{\cdot}S{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}OMe$, crystallised on cooling in flat needles, m. p. 160—161°. This was hydrolysed by warm 10% ammonia solution to *α-thiolaceto*-p-*anisidide*,

$$SH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}OMe,$$

stout needles, m. p. 116°, which was oxidised by ferric chloride to *dithiodiaceto*-p-*anisidide*, $(OMe{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2)_2S_2$, colourless needles, m. p. 185°. The thiol gave the following derivatives when heated with alkyl haloids and 0·5*N*-alcoholic potassium hydroxide: *α-methylthiolaceto*-p-*anisidide*, microscopic needles, m. p. 94°, *α-ethylthiolaceto*-p-*anisidide*, m. p. 68°, *α-isopropylthiolaceto*-p-*anisidide*, m. p. 58°, *α-isobutylthiolaceto*-p-*anisidide*, colourless leaflets, m. p. 86°, *α-benzylthiolaceto*-p-*anisidide*, $CH_2Ph{\cdot}S{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}OMe$, m. p. 82°. Similarly, ethylene dibromide, propylene dibromide, and trimethylene dibromide yielded *ethylenedithiolaceto*-p-*anisidide*,

$$(OMe{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}S)_2C_2H_4,$$

m. p. 177—178°, *propylenedithiolaceto*-p-*anisidide*,

$$(OMe{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}S{\cdot})_2C_3H_6,$$

m. p. 103°, and *trimethylenedithiolaceto*-p-*anisidide*,

$$(OMe{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}S{\cdot}CH_2)_2CH_2,$$

slender leaflets, m. p. 139°. Other products of condensations include *dimethylmethylenedithiolaceto*-p-*anisidide*,

$$(OMe{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}S{\cdot})_2CMe_2$$

(from acetone and hydrogen chloride), slender needles, m. p. 168°, *αβ'-hydroxyethylthiolaceto*-p-*anisidide*,

$$OH{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}OMe$$

(from ethylene chlorohydrin), m. p. 78°, *α-carbethoxythiolaceto*-p-*anisidide*,

$CO_2Et\cdot S\cdot CH_2\cdot CO\cdot NH\cdot C_6H_4\cdot OMe$ (from ethyl chloroformate), flat needles, m. p. 90°, *α-carbamylmethylthiolaceto-p-anisidide*, $NH_2\cdot CO\cdot CH_2\cdot S\cdot CH_2\cdot CO\cdot NH\cdot C_6H_4\cdot OMe$ (from chloroacetamide), m. p. 148°, and *α-α'-carboxyethylthiolaceto-p-anisidide*, $CO_2H\cdot CHMe\cdot S\cdot CH_2\cdot CO\cdot NH\cdot C_6H_4\cdot OMe$ (from α-bromopropionic acid), long, slender needles, m. p. 121°.

In the following derivatives of *p*-phenetidine, R = $\cdot NH\cdot C_6H_4\cdot OEt$.

α-Carbamylthiolaceto-p-phenetidide, $NH_2\cdot CO\cdot S\cdot CH_2\cdot CO\cdot R$, glistening leaflets, m. p. 123°, gave *α-thiolaceto-p-phenetidide*, $SH\cdot CH_2\cdot CO\cdot R$, leaflets, m. p. 117°, which was easily oxidised to *dithiodiaceto-p-phenetidide*, $(R\cdot CO\cdot CH_2)_2S_2$, m. p. 186°. The following derivatives of the thiol were prepared: *methyl-*, m. p. 63°, *ethyl-*, m. p. 87°, iso*propyl-*, m. p. 99—100°, iso*butyl-*, m. p. 106—107°, *benzyl-*, m. p. 111°, *ethylenedithiolaceto-p-phenetidide*, $C_2H_4(S\cdot CH_2\cdot CO\cdot R)_2$, m. p. 197°, the corresponding *propylene-*, m. p. 158°, *trimethylene-*, m. p. 147°, and *dimethylmethylene-*, m. p. 171°, compounds, *α-allylthiolaceto-p-phenetidide*, $C_3H_5\cdot S\cdot CH_2\cdot CO\cdot R$, m. p. 78°, *α-β'-hydroxyethyl-*, $OH\cdot CH_2\cdot CH_2\cdot S\cdot CH_2\cdot CO\cdot R$, m. p. 81°, *carbomethoxy-*, $CO_2Me\cdot S\cdot CH_2\cdot CO\cdot R$, m. p. 119°, *carbethoxy-*, m. p. 106°, *thioldiaceto-p-phenetidamic acid*, $CO_2H\cdot CH_2\cdot S\cdot CH_2\cdot CO\cdot R$, from chloroacetic acid, m. p. 114° (crystalline *barium* salt, *amide*, m. p. 155°, *ethyl* ester), and *α-α'-carboxyethylthiolaceto-p-phenetidide*, $CO_2H\cdot CHMe\cdot S\cdot CH_2\cdot CO\cdot R$, m. p. 113° (*barium* salt). J. C. W.

Toluidides of the Thiolbutyric Acids. H. Beckurts and G. Frerichs (with A. Strickrodt) (*Arch. Pharm.*, 1915, **253**, 155—181. Compare preceding abstract).—*o*-Toluidine, α-bromobutyric acid, and potassium thiocyanate, when heated in alcohol, gave *α-carbamylthiolbutyro-o-toluidide*, $NH_2\cdot CO\cdot S\cdot CHEt\cdot CO\cdot NH\cdot C_7H_7$, needles, m. p. 129°; the corresponding m-*toluidide*, m. p. 124°, and p-*toluidide*, m. p. 144°, were prepared in the same way. These were hydrolysed by 10% ammonia to *α-thiolbutyro-o-toluidide*, $SH\cdot CHEt\cdot CO\cdot NH\cdot C_7H_7$, long needles, m. p. 99°, the m-*toluidide*, m. p. 72°, and the p-*toluidide*, m. p. 77—78°, which, in turn, were oxidised to the *α-dithiodibutyrotoluidides*, $S_2(CHEt\cdot CO\cdot NH\cdot C_7H_7)_2$ (*ortho*, m. p. 139°, *meta*, m. p. 146°, *para*, m. p. 148—149°).

The thiols gave the following alkyl derivatives: *methyl*, $SMe\cdot CHEt\cdot CO\cdot NH\cdot C_7H_7$ (*ortho*, white needles, *meta*, m. p. 77°, *para*, m. p. 89°); *ethyl*, $C_{13}H_{19}ONS$ (*ortho*, m. p. 69°, *meta*, a viscous oil, *para*, m. p. 69—70°); *propyl*, $C_{14}H_{21}ONS$ (*ortho*, m. p. 66—67°, *meta*, a viscous oil, *para*, m. p. 68—69°); iso*propyl* (*ortho*, m. p. 74°, *meta*, solid below 0°, *para*, m. p. 118°); *benzyl*, $CH_2Ph\cdot S\cdot CHEt\cdot CO\cdot NH\cdot C_7H_7$ (*ortho*, m. p. 79—80°, *meta*, m. p. 83°, *para*, m. p. 75°). The condensation products with ethylene dibromide, namely, the *ethylenedi-α-thiolbutyrotoluidides*, $C_2H_4(S\cdot CHEt\cdot CO\cdot NH\cdot C_7H_7)_2$, were as follows: *ortho*, m. p. 158°, *meta*, m. p. 114°, *para*, m. p. 202°. The *dimethylmethylenedi-α-thiolbutyrotoluidides*, $CMe_2(S\cdot CHEt\cdot CO\cdot NH\cdot C_7H_7)_2$,

obtained by condensing the thiols with acetone, had the m. p.'s, *ortho*-147—148°, *meta* 153°, *para* 154—155°. The *α-carbomethoxythiolbutyrotoluidides*, $CO_2Me{\cdot}S{\cdot}CHEt{\cdot}CO{\cdot}NH{\cdot}C_7H_7$, obtained from methyl chlorocarbonate, formed needles (*ortho*, m. p. 64—65°, *meta*, m. p. 87°, *para*, m. p. 74—75°), and the *carbethoxy*-compounds had the m. p.'s, *ortho*, 101°, *meta*, somewhat low, *para*, 81°. The thiols were also condensed with chloroacetic acid, ethyl chloroacetate, chloroacetamide, and α-chloroacetanilide, yielding: the *α-α'-carboxymethylthiolbutyrotoluidides*, $CO_2H{\cdot}CH_2{\cdot}S{\cdot}CHEt{\cdot}CO{\cdot}NH{\cdot}C_7H_7$ (*ortho*, m. p. 113°, *meta*, m. p .118°, *para*, a soft mass which gave a crystalline barium salt); the corresponding *ethyl* esters, $CO_2Et{\cdot}CH_2{\cdot}S{\cdot}CHEt{\cdot}CO{\cdot}NH{\cdot}C_7H_7$ (*ortho*, white needles, *meta*, a yellow, viscous oil, *para*, tufts of needles, m. p. 47—48°); the *amides*,

$$NH_2{\cdot}CO{\cdot}CH_2{\cdot}S{\cdot}CHEt{\cdot}CO{\cdot}NH{\cdot}C_7H_7$$

(*ortho*, m. p. 149°, *meta*, m. p. 122—123°, *para*, m. p. 139—140°), and the *anilides*, $NHPh{\cdot}CO{\cdot}CH_2{\cdot}S{\cdot}CHEt{\cdot}CO{\cdot}NH{\cdot}C_7H_7$ (*ortho*, m. p. 163—164°, *meta*, m. p. 157—158°, *para*, m. p. 135—136°). J. C. W.

Nitrotolylglycines. WILHELM POLLAK (*J. pr. Chem.*, 1915, [ii], **91**, 285—306).—An account of the preparation of a number of nitrotolyl glycines from bromoacetic acid and nitrotoluidines.

5-*Nitro*-o-*toluidinoacetic acid*, $NO_2{\cdot}C_6H_3Me{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, prepared by heating 4-nitro-*o*-toluidine with bromoacetic acid for two to three hours at 120°, crystallises in light yellow, lustrous needles, m. p. 140°, and yields a *silver* salt, crystallising with $\frac{1}{2}H_2O$ in light yellow needles, which become orange when kept; the *cupric* salt separates with $1H_2O$ in light green crystals, m. p. 195°. The *methyl* ester, prepared from the silver salt and methyl iodide, crystallises in light yellow needles, m. p. 108°; the *ethyl* ester, obtained by direct esterification of the acid, forms reddish-brown needles, m. p. 42°. On reduction with stannous chloride or tin and hydrochloric acid, the acid is converted into 5-*amino*-o-*toluidinoacetic acid*, the *hydrochloride* of which forms brown crystals, m. p. 98°. When heated at 150—160°, it yields 2 : 5-*diketo*-1 : 4-*di*-(5-*nitro*-o-*tolyl*)*piperazine*, m. p. 186°,

$$NO_2{\cdot}C_6H_3Me{\cdot}N\begin{matrix}CO{\cdot}CH_2\\ CH_2{\cdot}CO\end{matrix}N{\cdot}C_6H_3Me{\cdot}NO_2.$$

m-*Nitro*-p-*toluidinoacetic acid*, prepared from 2-nitro-*p*-toluidine and bromoacetic acid, crystallises in yellow prisms, m. p. 130°; the *ammonium* (reddish-brown prisms, m. p. 135°), *lead*, PbA_2,H_2O (microscopic, orange needles), and *cupric*, CuA_2,H_2O (m. p. 160°) salts are described.

3-*Nitro*-o-*toluidinoacetic acid*, from 6-nitro-*o*-toluidine, forms stout, yellowish-brown, prismatic crystals, m. p. 152°, and yields grey salts, of which the *silver*, *ammonium* and *lead* (PbA_2,H_2O, m. p. 170°) salts were prepared.

4-*Nitro*-o-*toluidinoacetic acid*, from 5-nitro-*o*-toluidine and bromoacetic acid at 120—130°, separates from alcohol in ill-defined reddish-brown crystals; the *potassium* salt is dark red, the *lead* salt light yellow, and *barium* salt, $BaA_2,\frac{1}{2}H_2O$ (needles), yellowish-brown; most of the salts, especially the *silver* salt, are explosive; the *nitroso*-derivative, $NO_2{\cdot}C_6H_3Me{\cdot}N(NO){\cdot}CH_2{\cdot}CO_2H$, has m. p. 110°. The *ethyl* ester,

prepared by heating 5-nitro-*o*-toluidine with ethyl chloroacetate at 130—140° in alcoholic solution, has m. p. 87°; the *methyl* ester, obtained by directly esterifying the acid, forms yellow needles, m. p. 82°.

p-*Nitro*-m-*toluidinoacetic acid*, from 6-nitro-*m*-toluidine and bromoacetic acid, has m. p. 145° and forms well crystallised salts with most bases.

Attempts to condense 3-nitro-*o*-toluidine with bromoacetic acid were unsuccessful. F. B.

Resolution of Externally Compensated *p*-Toluenesulphonylalanine into its Optically Active Components. CHARLES STANLEY GIBSON and JOHN LIONEL SIMONSEN (T., 1915, **107**, 798—803. Compare Pope and Gibson, T., 1912, **101**, 939).—*dl*-*p*-Toluenesulphonylalanine has been resolved by the equilibrium method in two ways, namely, by using first strychnine and then brucine, and by using these alkaloids in the reverse order. The resolution is completely reversible and is not complicated by the formation of mixed crystals.

l-p-*Toluenesulphonylalanine* forms long, colourless needles, m. p. 131—132°, $[\alpha]_{5461}^{29-30°}$ varying from −33·8° to −40·08° for $c = 0·673 - 6·681$ as sodium salt in aqueous solution; the *brucine* salt crystallises with $3H_2O$ in large, brittle, colourless, glistening plates, m. p. 148—149°, $[\alpha]_{5461}^{29-30°}$ −38·51° in alcohol.

The d-*isomeride* has similar properties and forms a *strychnine* salt, crystallising with $2H_2O$ in large, colourless, glistening prisms, which lose $1H_2O$ at 125°, m. p. 188—189°, $[\alpha]_{5461}^{29-30°}$ −11·2° in aqueous solution. F. B.

Hyposulphites. IX. Sulphones from Rongalite. A. BINZ, O. LIMPACH and W. JANNSEN (*Ber.*, 1915, **48**, 1069—1077. Compare Binz and Marx, A., 1910, i, 711, 728).—In an earlier communication (Binz and Isaac, A., 1908, i, 941) of the results of an investigaton of rongalite (sodium formaldehydesulphoxylate) it was stated that the condensation product, m. p. 199°, obtained by heating together rongalite, formaldehyde and dimethylaniline hydrochloride in aqueous solution was a tetramethyldiaminophenylbenzylsulphone,

$$NMe_2 \cdot C_6H_4 \cdot CH_2 \cdot SO_2 \cdot C_6H_4 \cdot NMe_2.$$

It is now found that the molecule is symmetrical, the compound being a tetramethyldiaminodibenzylsulphone, the chemical change proceeding according to the equation $2NPhMe_2 + OH \cdot CH_2 \cdot SO_2Na + HCl + CH_2O =$

$$SO_2(CH_2 \cdot C_6H_4 \cdot NMe_2)_2 + NaCl + 2H_2O.$$

s-Tetramethyldiaminodibenzylsulphone forms a *picrate*, crystals, m. p. 170°, and is converted by methyl sulphate into a quaternary ammonium *sulphate*, $SO_2(CH_2 \cdot C_6H_4 \cdot NMe_3 \cdot SO_4Me)_2$, scales, m. p. 259°. Treatment with a mixture of sulphuric and nitric acids produces a *dinitro*-compound, $SO_2[CH_2 \cdot C_6H_3(NO_2) \cdot NMe_2]_2$, yellowish-brown needles, m. p. 191°, which is reducible by tin and hydrochloric acid to a *tetramethyltetra-aminodibenzylsulphone*, $SO_2[CH_2 \cdot C_6H_3(NH_2) \cdot NMe_2]_2$, needles, m. p. 184°. A mixture of hydrogen peroxide and hydrochloric acid converts the parent compound into a *chloro*-derivative,

$$NMe_2 \cdot C_6H_3Cl \cdot CH_2 \cdot SO_2 \cdot CH_2 \cdot C_6H_4 \cdot NMe_2,$$

needles, m. p. 162—164°.

s-*Tetraethyldiaminodibenzylsulphone*, $SO_2(CH_2 \cdot C_6H_4 \cdot NEt_2)_2$, leaflets, m. p. 162—163°, was obtained in a similar manner, but not quite so easily as the tetramethyl analogue; under treatment with hydrogen peroxide and hydrochloric acid, it was converted into a *dichloro*-derivative, $SO_2(CH_2 \cdot C_6H_3Cl \cdot NEt_2)_2$, needles, m. p. 97—98°.

In the interaction of rongalite, aniline hydrochloride and formaldehyde in hot aqueous solution, it is probable that the primary product undergoes a benzidine rearrangement, because the isolated product is 4 : 4′-*diaminodibenzylsulphone*, $SO_2(CH_2 \cdot C_6H_4 \cdot NH_2)_2$, *diacetyl* derivative, crystals, m. p. 281°. Toluene likewise gave rise to a non-crystalline 4 : 4′-*diaminodi*-3 : 3′-*dimethyldibenzylsulphone*,

$$SO_2(CH_2 \cdot C_6H_4Me \cdot NH_2)_2;$$

diacetyl derivative, silky needles, m. p. 274°. *o*-Anisidine similarly gave 4 : 4′-*diamino*-3 : 3′-*dimethoxydibenzylsulphone*,

$$SO_2[CH_2 \cdot C_6H_4(OMe) \cdot NH_2]_2,$$

yellowish-green prisms, m. p. 184—185°.

The above sulphones eliminate their characteristic $-SO_2 \cdot$ group when heated with amines or phenols, the products being diphenylmethane derivatives. Thus, if tetramethyldiaminodibenzylsulphone is heated to boiling with a mixture of aniline and aniline hydrochloride, sulphur dioxide is liberated, and the product is *as*-dimethyl-4 : 4′-diaminodiphenylmethane, $CH_2(C_6H_4 \cdot NH_2)_2$, m. p. 90—91°; *benzylidene* derivative, pale yellow needles, m. p. 90°. The same sulphone when heated with *o*-toluidine hydrochloride and lead acetate yielded *as*-dimethyl-4 : 4′-diaminophenyl-*m*-tolylmethane,

$$NMe_2 \cdot C_6H_4 \cdot CH_2 \cdot C_6H_3Me \cdot NH_2,$$

m. p. 93—94°; tetra-ethyldiaminodibenzylsulphone gave the corresponding *as*-diethyl-4 : 4′-diaminophenyl-*m*-tolylmethane, m. p. 59—60°.

The action of α-naphthol and of β-naphthol on tetramethyldiaminodibenzylsulphone in boiling cumene solution gave rise respectively to *dimethyl*-p-*aminophenyl*-α-*hydroxynaphthylmethane*,

$$NMe_2 \cdot C_6H_4 \cdot CH_2 \cdot C_{10}H_6 \cdot OH,$$

needles, m. p. 149°, and its β-hydroxy-*isomeride*, crystals, m. p. 144—145°. D. F. T.

The Quaternary Salts of Hexamethylenetetramine. VI. Halogenethyl Ethers and Esters and their Hexamethylenetetraminium Salts. Walter A. Jacobs and Michael Heidelberger (*J. Biol. Chem.*, 1915, **21**, 439—453).—An account of the preparation of a number of β-bromoethyl ethers and esters, and their additive compounds with hexamethylenetetramine.

β-Phenoxyethylhexamethylenetetraminium bromide, $C_{14}H_{21}ON_4Br$, prepared from phenyl β-bromoethyl ether and hexamethylenetetramine in boiling chloroform solution, has m. p. 151—152°.

β-o-Tolyloxyethylhexamethylenetetraminium bromide, from *o*-tolyl β-bromoethyl ether, forms glistening prisms and plates, m. p. 185°.

m-*Tolyl β-bromoethyl ether*, obtained as a colourless oil, b. p. 136—137°/14 mm., by heating ethylene dibromide and *m*-cresol with alcoholic sodium hydroxide, yields a hexamethylenetetramine *compound*, $C_{15}H_{23}ON_4Br$, m. p. 155—156°.

β-p-*Tolyloxyhexamethylenetetraminium bromide* has m. p. 176°.

α-Naphthyl β-bromoethyl ether, prepared from α-naphthol and ethylene dibromide in the same manner as the *m*-tolyl ether, crystallises in transparent, hexagonal plates, m. p. 25° (corr.) with slight preliminary softening, b. p. 154—156°/0·8 mm., and yields a hexamethylenetetramine *compound*, crystallising in glistening platelets, which become yellow at 170°, m. p. 175° (decomp.).

β : 2-*Naphthoxyethylhexamethylenetetraminium bromide* crystallises from chloroform in glistening leaflets of the composition

$$C_{18}H_{23}ON_4Br,\tfrac{1}{2}CHCl_3$$

(decomp. about 180°).

2 : 4 : 6-*Trichlorophenyl β-bromoethyl ether*, prepared from 2 : 4 : 6-trichlorophenol and ethylene dibromide, has m. p. 47—48° (corr.), and reacts with diethylamine, yielding *β*-2 : 4 : 6-*trichlorophenoxyethyldimethylamine*, $C_6H_2Br_2\cdot O\cdot CH_2\cdot CH_2\cdot NMe_2$, the *hydrochloride* of which forms long, silky needles, m. p. 187—189°; when heated with piperidine in benzene solution, it yields N-2 : 4 : 6-*trichloro-β-phenoxyethylpiperidine*, $C_6H_2Br_2\cdot O\cdot CH_2\cdot CH_2\cdot C_5H_{10}N$, which was isolated in the form of its *hydrochloride*, m. p. 188—189°.

p-*Bromophenyl β-bromoethyl ether*, obtained by brominating phenyl *β*-bromoethyl ether in chloroform solution, crystallises in rhombs, m. p. 56—57° (corr.) with slight preliminary softening, and forms a hexamethylenetetramine *compound* (decomp. 185—186°).

Tribromo-p-*tolyl β-bromoethyl ether*, prepared from tribromo-*p*-cresol and ethylene dibromide, has m. p. 50—51° (corr.) with preliminary softening, forms a hexamethylenetetramine *compound*, m. p. 181°, and reacts with piperidine in boiling benzene solutions, yielding N-*tribromo-β*-p-*tolyloxyethylpiperidine*, $C_6HMeBr_3\cdot O\cdot CH_2\cdot CH_2\cdot C_5H_{10}N$, the *hydrobromide* of which has m. p. 223—230° (decomp.). In one preparation in which an impure tribromo-*p*-cresol, containing apparently some tetrabromocresol, was employed, a small amount of *tetrabromo*-p-*tolyl β-bromoethyl ether* was isolated in glistening needles, m. p. 106—107·5° with preliminary softening.

o-*Acetylamino-β-phenoxyethyl bromide*, $NHAc\cdot C_6H_4\cdot O\cdot CH_2\cdot CH_2Br$, prepared from *o*-acetylaminophenol and ethylene dibromide in boiling alcoholic sodium hydroxide solution, forms needles, m. p. 90—90·5° (corr.) with preliminary softening, yields a hexamethylenetetramine *compound*, m. p. 160°, and is hydrolysed by hydrobromic acid to o-*amino-β-phenoxyethyl bromide*, which crystallises in glistening leaflets, m. p. 36—37° (corr.), and yields a *hydrobromide*, long needles, m. p. 193—198° (decomp.). When heated with piperidine in benzene solution and the resulting product hydrolysed with hydrochloric acid, it is converted into N-o-*amino-β-phenoxyethylpiperidine hydrochloride*, short, thick prisms, m. p. 184—185·5°, from which the free *base*, $NH_2\cdot C_6H_4\cdot O\cdot CH_2\cdot CH_2\cdot C_5H_{10}N$, crystallising in diamond-shaped plates, m. p. 69—70° (corr.) with preliminary softening, is liberated by sodium carbonate.

p-*Acetylamino-β-phenoxyethylhexamethylenetetraminium bromide* has m. p. 196—198°.

Methyl salicylate reacts with ethylene dibromide and aqueous alcoholic sodium hydroxide, yielding *methyl* o-*β-bromoethoxybenzoate*,

$CH_2Br\cdot CH_2\cdot O\cdot C_6H_4\cdot CO_2Me$, large, thick, transparent plates, m. p. 37·5—38° (corr.), b. p. 186—188°/20 mm.

o-*β-Bromoethoxybenzamide*, prepared from salicylamide in a similar manner, using alcoholic sodium ethoxide, has m. p. 112—114°, and is accompanied by *salicylamide ethylene ether*, $C_2H_4(O\cdot C_6H_4\cdot CO\cdot NH_2)_2$, m. p. 211·5° (corr.).

β-Acetoxyethylhexamethylenetetraminium bromide, obtained from β-bromoethyl acetate (ethylene bromoacetin) and hexamethylenetetramine, forms silky needles, m. p. 172—173°.

β-Benzoyloxyethylhexamethylenetetraminium bromide, from β-bromoethyl benzoate, crystallises in glistening needles, and melts at 164—165° to a yellow paste.

β-Bromoethyl-p-*nitrobenzoate* is obtained in faintly yellow, rhombic crystals, m. p. 47—50° (corr.), by heating ethylene bromohydrin with *p*-nitrobenzoyl chloride at 140°; the *hexamethylenetetramine compound* crystallises in glistening leaflets, m. p. 190—191° (decomp.).

p-*Nitro-β-benzoyloxyethylhexamethylenetetraminium iodide*, prepared from *β-iodoethyl* p-*nitrobenzoate*, forms glistening, yellow platelets, m. p. 176—178°.

The following β-bromoethyl esters were obtained by the interaction of the acid chlorides and ethylene bromohydrin in pyridine solution: o-*acetoxybenzoate*, $OAc\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2Br$, thick plates and prisms, m. p. 62—62·5° (corr.) with preliminary softening, b. p. 150—160°/0·7 mm.; *acetyl*-p-*cresotate* [4-*acetoxy*-m-*toluate*], delicate, glistening needles, m. p. 62·5—63° (corr.) with preliminary softening; m-*chloroacetylaminomethylbenzoate*,

$$CH_2Cl\cdot CO\cdot NH\cdot CH_2\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2Br,$$

minute, pale yellow prisms, m. p. 107—108·5° (corr.).

β-Bromoethyl-p-*methoxybenzoate* has b. p. 140° (corr.)/0·5 mm., 189—191°/14 mm. F. B.

m-Nitrophenyl Thiocyanate and Allied Compounds. Fr. Fichter and Rudolf Schonlau (*Ber.*, 1915, **48**, 1150—1154).—An extension of the investigation of the electrolytic reduction of *o*-, *p*-, and 2 : 4-dinitrophenyl thiocyanates (Fichter and Beck, A., 1912, i, 105).

The preparation of m-*nitrophenyl thiocyanate*, $NO_2\cdot C_6H_4\cdot SCN$, from diazotised *m*-nitroaniline solution, thiocyanic acid, and cuprous thiocyanate proceeds less smoothly than that of its isomerides; the product, colourless needles, m. p. 56°, when reduced at a rotating lead cathode in 7*N*-alcoholic hydrogen chloride solution and subsequently submitted to gentle oxidation by atmospheric oxygen or ferric chloride, gave 3 : 3′-diaminodiphenyl disulphide, $S_2(C_6H_4\cdot NH_2)_2$. With high concentrations of acid, a copper electrode gives a similar result, but in 2*N*-alcoholic hydrogen chloride, m-*thiocyanatoazoxybenzene*,

$$ON_2(C_6H_4\cdot SCN)_2,$$

yellow needles, m. p. 96°, was obtained.

In the earlier investigation (Fichter and Beck, *loc. cit.*), *o*-nitrophenyl thiocyanate was found to undergo reduction with formation of 2-aminobenzothiazole, $C_6H_4\langle{}^{N}_{S}\rangle C\cdot NH_2$, but the explanation that this

is due to the condensation of *o*-aminophenyl mercaptan and hydrocyanic acid previously produced is now withdrawn, because condensation of *o*-aminophenyl mercaptan with hydrocyanic acid yields benzothiazole. In the formation of 2-aminobenzothiazole it is the 2 : 2′-diamino-disulphide, produced by oxidation of the corresponding mercaptan, which is active, its condensation with hydrocyanic acid yielding 2-aminobenzothiazole and benzothiazole.

Electrolytic oxidation of methyl and methylene thiocyanates in a mixture of acetic and hydrochloric acids proceeds analogously to that of the ethyl compound (Fichter and Wenk, A., 1912, i, 423), the corresponding sulphonic acids being produced; the preparation is somewhat disturbed by the ease with which these acids undergo further oxidation at the platinum anode. With phenyl thiocyanate and *o*-nitrophenyl thiocyanate, resinous products were obtained, the aromatic nucleus being attacked (compare Fichter and Stocker, A., 1914, i, 946). D. F. T.

6-Chloro- and 6-Bromo-*m*-cresol. I. R. (Fhr.) von Walther and W. Zipper (*J. pr. Chem.*, 1915, [ii], **91**, 364—414).—An account of the preparation and properties of a number of derivatives of 6-chloro- and 6-bromo-*m*-cresol and of *p*-chloro-*m*-cresotic [6-chloro-3-hydroxy-*p*-toluic] acid.

On treatment with chlorine in cold glacial acetic acid solution, *m*-cresol gives rise to 2 : 4 : 6-trichloro-*m*-cresol, m. p. 45° (compare Raiford, A., 1911, i, 993; Crowther and McCombie, T., 1913, **103**, 536), and 2 : 4 : 5-*trichloro*-1-*chloromethyl*-p-*benzoquinone dichloride* [2 : 4 : 4 : 5 : 6-*pentachloro*-3-*chloromethyl*-$\Delta^{2:5}$-cyclo*hexadienone*], $CH_2Cl\cdot C\lessdot\begin{matrix}CCl—CO\\CCl_2\cdot CCl\end{matrix}\gtrdot CCl$, crystallising in prisms, m. p. 117°. The last-named compound, together with 2 : 4 : 5-trichloro-*p*-toluoquinone and 2 : 4 : 4 : 5 : 6-pentachloro-3-methyl-$\Delta^{2:5}$-*cyclo*hexadienone, m. p. 89—90° (compare Crowther and McCombie, *loc. cit.*), is also produced by chlorinating *m*-cresol in glacial acetic acid at 100°.

4 : 6-Dichloro-*m*-cresol, m. p. 45—46°, is readily obtained by passing the calculated amount of chlorine into a warm solution of 6-chloro-*m*-cresol in aqueous sodium hydrogen carbonate (compare Claus and Schweitzer, A., 1886, 614).

6-*Bromo*-m-*cresol*, prepared by the addition of the calculated amount of bromine to *m*-cresol in carbon tetrachloride solution at −5° to −10°, crystallises in long, white needles, m. p. 62°; solubility in water at 19° = 0·1713 gram per 100 c.c.; the *benzoyl* derivative, prepared in pyridine solution, forms needles, m. p. 83—83·5°.

6-*Chloro*-4-*bromo*-m-*cresol*, m. p. 70—70·5°, and 6-*chloro*-2 : 4-*dibromo*-m-*cresol* m. p. 70—70·5°, obtained by brominating 6-chloro-*m*-cresol in carbon tetrachloride and glacial acetic acid respectively, crystallise in white needles.

p-Chloro-*m*-cresotic [6-chloro-3-hydroxy-*p*-toluic] acid is readily prepared by heating the anhydrous *sodium* salt of 6-chloro-*m*-cresol with carbon dioxide under pressure at 160—175°. It crystallises in needles or leaflets, m. p. 206—207° (solubility in water at 12° = 0·0120 gram per 100 c.c.), gives a bluish-violet coloration with ferric chloride, and

may also be obtained, together with small quantities of 2 : 4 : 5-trichloro-*p*-toluoquinone, 2 : 4 : 4 : 5 : 6-pentachloro-3-chloromethyl-$\Delta^{2:5}$-*cyclo*hexadienone and 2 : 4 : 4 : 5 : 6-pentachloro-3-methyl-$\Delta^{2:5}$-*cyclo*hexadienone by the direct chlorination of *m*-cresotic [3-hydroxy-*p*-toluic] acid in glacial acetic acid solution. The *methyl* ester, white leaflets, m. p. 55°, ethyl ester, leaflets, m. p. 52·5—53°, *propyl* ester, prisms, m. p. 21°, b. p. 168—170°/18 mm., together with the following salts are described: *sodium*, leaflets; *potassium*, microscopic needles or white prisms; *lithium*, needles; *ammonium*, white needles; *calcium*, leaflets; *barium*, leaflets; *silver*, microscopic, white needles; *lead*, *mercuric*, *ferric*, *aluminium*; *magnesium*, leaflets; *manganese*, microscopic needles; basic *cupric*, olive leaflets; *bismuth*.

The *hexamethylenetetramine*, $C_8H_7O_3Cl,C_6H_{12}N_4$, salt, prepared in alcoholic solution, crystallises in prisms, which become pale yellow at 160°, m. p. 170° (decomp.), and give blue fluorescent solutions in aqueous sodium hydroxide; the *antipyrine*, needles, m. p. 128°, *quinine*, and *cinchonine* salts are also described.

6-Bromo-3-hydroxy-*p*-toluic acid, prepared by brominating *m*-cresotic acid in carbon tetrachloride solution, crystallises in lustrous leaflets or rectangular columns capped with pyramids, m. p. 221° and not 211° as given by Gatterman (A., 1893, i, 566); the *alkali*, *ammonium*, *cobalt*, *magnesium*, *barium*, *silver*, *mercury*, *lead*, *gold*, *platinum*, *ferric* and *copper* salts are mentioned.

Methyl 6-*chloro*-3-*methoxy*-p-*toluate* is obtained by heating (1) the *sodium* salt of methyl 3-chloro-3-hydroxy-*p*-toluate with methyl iodide at 130°, or (2) the disodium salt of the free hydroxy-acid with methyl sulphate in aqueous sodium hydroxide, solution, crystallises in pale yellow needles, m. p. 53—54°, b. p. 160°/14 mm., and is hydrolysed by sodium hydroxide to the free *acid*, prisms, m. p. 130°, of which the readily soluble *alkali* and *ammonium*, sparingly soluble, white *calcium*, *barium*, *lead*, yellow *ferric* and light blue *cupric* salts are described.

The following acids were all prepared by heating the sodium salt of 6-chloro-3-hydroxy-*p*-toluate with the requisite alkyl iodide and subsequent hydrolysis of the resulting esters with sodium hydroxide:

6-*Chloro*-3-*ethoxy*-p-*toluic acid*, needles, m. p. 143°; *methyl* ester, slender, felted, pale yellow needles, m. p. 54°, b. p. 170°/11 mm.

6-*Chloro*-3-*propoxy*-p-*toluic acid*, long, white needles or broad prisms, m. p. 112°; *methyl* ester, colourless oil, b. p. 188°/24 mm.

6-*Chloro*-3-iso*propoxy*-p-*toluic acid*, long, narrow prisms, m. p. 121°; *methyl* ester, colourless, strongly refractive oil, b. p. 173°/19 mm.

6-*Chloro*-3-*butyloxy*-p-*toluic acid*, needles, m. p. 96·5°; *methyl* ester, b. p. 194°/20 mm.

6-*Chloro*-3-iso*butyloxy*-p-*toluic acid* (m. p. 117°?), not obtained in pure condition; *methyl* ester, strongly refractive oil, b. p. 187°/14 mm., which solidifies in long prisms.

6-*Chloro*-3-iso*amyloxy*-p-*toluic acid*, leaflets, m. p. 94°; *methyl* ester, b. p. 197°/18 mm.

When heated on the water-bath with methyl alcoholic sodium methoxide and methyl ulphate, 6-bromo-3-hydroxy-*p*-toluic acid is converted into its *methyl* ester, white needles, m. p. 48°, which is

accompanied by *methyl* 6-*bromo*-3-*methoxy*-p-*toluate*, long leaflets, m. p. 45—46°.

6-*Chloro*-m-*tolyl* *salicylate*, prepared by heating salicylic acid and 4-chloro-*m*-cresol with phosphoryl chloride at 135—140°, crystallises in slender needles, m. p. 74°.

6-*Chloro*-m-*tolyl* 6-*chloro*-3-*hydroxy*-p-*toluate*, obtained in a similar manner from *p*-chloro-*m*-cresotic acid, forms microscopic needles, m. p. 142°; the *phenyl* ester crystallises in needles, m. p. 88°; the *β-naphthyl* ester in prisms, m. p. 137·5°.

The rate of hydrolysis of the four last-named esters by methyl alcoholic sodium hydroxide at 30° has been determined and found to be about the same as that of phenyl salicylate.

6-*Chloro*-3-*acetoxy*-p-*toluic acid*, prepared from the corresponding hydroxy-acid and acetyl chloride at 70—80°, crystallises in sheaves of colourless needles, m. p. 146°, and on treatment with thionyl chloride is converted into the *chloride*, $CH_3 \cdot CO_2 \cdot C_6H_2Cl(OH) \cdot COCl$, long needles, m. p. 48°, from which the following derivatives were prepared: *phenyl* ester, white needles, m. p. 88°; *amide*, white leaflets, m. p. 239—240°; *anilide*, leaflets, m. p. 222°; p-*phenetidide*, leaflets, m. p. 215°.

6-*Bromo*-3-*acetoxy*-p-*toluic acid*, obtained in a similar manner, forms white leaflets, m. p. 155°. On treatment with the calculated amount of dilute nitric acid in 80% acetic acid solution, 6-chloro-*m*-cresol yields 6-*chloro*-4-*nitro*-m-*cresol*, which crystallises in yellow leaflets, m. p. 133·5°, and gives rise to the following salts: *ammonium*, orange-yellow leaflets, m. p. 146° (decomp.); *sodium*, red needles; *potassium*, dark red leaflets; *barium*, red leaflets; *calcium*, orange-red needles; *mercuric*, pale brownish-yellow leaflets; *cupric*, light green leaflets; *ferric*, yellow to dark brown, feathery crystals; *aluminium*, yellow, feathery crystals; the *lead* salt is brick-red, the *chromium* light green; the *silver*, *gold*, and *platinum* salts form yellow leaflets; *aniline* salt, citron-yellow leaflets, m. p. 134°; the o- and p-*toluidine* salts, light yellow leaflets, m. p. 132° and 133° respectively.

The mononitro-derivative is accompanied by 6-*chloro*-2 : 4-*dinitro*-m-*cresol*, which crystallises in yellow leaflets, m. p. 69°, and yields the following salts: *sodium* (orange); *potassium*, orange needles; *calcium*, golden-yellow leaflets; *barium*, microscopic, orange needles; *mercury*, reddish-brown needles; *cupric* and *lead*, brown needles; *ferric* and *aluminium*, brown leaflets; *chromium*; *silver*, *gold*, and *platinum*, yellow needles; *aniline*, orange-yellow, microscopic needles, m. p. 136°; o- and p-*toluidine* salts, orange-yellow needles, m. p. 78° and 145° respectively.

6-*Chloro*-4-*amino*-m-*cresol*, prepared by reducing the corresponding nitro-compound with sodium hyposulphite, forms slender, white leaflets, m. p. 143°. F. B.

Nitration of 3-Acetylamino-2-methoxytoluene. John Lionel Simonsen and Mudlagiri Nayak (T., 1915, **107**, 828—834).—With the object of synthesising ultimately the isomeric nitro-2 : 3-dimethoxybenzoic acids by a method which would leave no doubt as to their

constitution (compare Cain and Simonsen, T., 1914, **105**, 156; Perkin and Robinson, *ibid.*, 2390), the authors have investigated the nitration of 3-acetylamino-2-methoxytoluene by means of fuming nitric acid (D 1·52) at a low temperature, and find that all three possible mononitro-derivatives are produced, the main product consisting of 6-nitro-3-acetylamino-2-methoxytoluene, whilst the 4-nitro-derivative is formed to only a small extent. The isomerides were separated by a complicated process, fully described in the original, and hydrolysed by concentrated hydrochloric acid to the free amines. Attempts to replace the amino-group in 5-nitro- and 6-nitro-3-amino-2-methoxytoluene by a hydroxyl group were unsuccessful, the sole product consisting of the corresponding nitro-2-methoxytoluene, formed by elimination of the amino-group.

3-*Acetylamino*-2-*methoxytoluene*, prepared by acetylating the free amine with acetic anhydride, crystallises in needles, m. p. 100—101°. 6-*Nitro*-3-*amino*-2-*methoxytoluene* forms massive, pale yellow rhomboids, m. p. 103°, the *acetyl* derivative, slender needles, m. p. 119—120°. Its constitution has been established (1) by its reduction to a *diamine* (not isolated in a pure condition), showing all the properties of a para-diamine, and (2) by its conversion, after diazotisation, into 6-*nitro*-2-*methoxytoluene*, needles, m. p. 52—53°; during the diazotisation a small amount of 6-nitro-*o*-cresol, m. p. 143° (compare Ullmann, A., 1884, 1317), is simultaneously produced, which on methylation with methyl sulphate yields 6-nitro-2-methoxytoluene.

5-*Nitro*-3-*amino*-2-*methoxytoluene*, slender, sulphur-yellow needles, m. p. 113°, forms a sparingly soluble *hydrochloride*, and is reduced to an unstable *diamine*, having the usual properties of a meta-diamine; the *acetyl* derivative, m. p. 141—142° in the anhydrous condition, crystallises with $1H_2O$ in long, irridescent, prismatic needles, decomp. 127°. Elimination of the amino-group by diazotisation and boiling with zinc dust results in the formation of 5-*nitro*-2-*methoxytoluene*, colourless needles, m. p. 63°, the constitution of which has been determined by its formation from 5-nitro-*o*-cresol by methylation.

4-*Nitro*-3-*amino*-2-*methoxytoluene* crystallises in deep orange-coloured, prismatic needles, m. p. 72°; the *acetyl* derivative in hexagonal prisms, m. p. 170—171°. F. B.

Preparation of *m*-5-Xylenol-4-sulphonic Acid. F. Raschig (D.R.-P. 283306; from *J. Soc. Chem. Ind.*, 1915, **34**, 708).—*m*-5-Xylenol when heated with concentrated sulphuric acid or other sulphonating agent is converted into the *ortho*-sulphonic acid, which, on account of the *para*-position to the hydroxyl group being unoccupied, exhibits great reactivity. It is very soluble in water, and is reprecipitated from strong solutions by concentrated hydrochloric acid in colourless needles, m. p. 102—103°. G. F. M.

β-Naphthol Sulphide and *iso*Sulphide. II. O. Hinsberg (*J. pr. Chem.*, 1915, [ii], **91**, 307—324).—An extension and amplification of previous work (this vol., i, 237).

Whilst β-naphthol sulphide dissolves readily in warm aqueous sodium carbonate, the *iso*-sulphide dissolves only to a slight extent, even on boiling, the solubility being due to conversion into the isomeric

β-naphthol sulphide. The transformation of the *iso*-sulphide into β-naphthol sulphide by warm aqueous sodium hydroxide may be almost entirely prevented by the addition of a little sodium sulphide.

iso-β-Naphthol sulphide is best characterised by its *di-β-naphthalenesulphonyl* derivative, $S(C_{10}H_6{\cdot}O{\cdot}SO_2{\cdot}C_{10}H_7)_2$, which separates from glacial acetic acid as a light yellow, crystalline powder containing solvent of crystallisation ($\frac{1}{2}$ mol.), m. p. 110° (decomp.) with previous sintering at 85°, and is readily obtained from the *iso*-sulphide and β-naphthalenesulphonyl chloride in pyridine solution.

When reduced with zinc dust and glacial acetic acid, and the resulting solution exposed to air, β-naphtholsulphoxide yields β-naphthol and β-naphthol disulphide, which forms yellow needles, m. p. 171° (compare Onufrowicz, A., 1891, 320), and gives a green coloration with ferric chloride. It is probable that the sulphoxide is first reduced to β-naphthol and 1-thiol-β-naphthol, and that the latter compound then undergoes atmospheric oxidation into the disulphide. On treatment with hydriodic acid or methyl alcoholic hydrogen chloride at the ordinary temperature, the sulphoxide is converted into β-naphthol and sulphur dioxide.

Dehydro-β-naphthol sulphide reacts with phenylhydrazine to form a monophenylhydrazone and not a dihydrazone as stated by Henriques (A., 1895, i, 104); the p-*nitrophenylhydrazone* crystallises in red needles, m. p. 207°; the *semicarbazone*, $C_{26}H_{17}O_3N_3$, forms brownish-red crystals (decomp. 175°). In view of the formation of these monoderivatives, the author abandons his previous formulæ for this compound, and assigns to it the constitutiou of an iso-*β-naphtholsulphonium anhydride*, $O{:}C_{10}H_6{:}S{<}\overset{C_{10}H_6}{O}$.

When kept for several days at the ordinary temperature in contact with methyl alcoholic hydrogen chloride, it is converted into Christopher and Smiles's chloronaphthathioxin; the latter compound obviously belongs to the *iso*-series, and is therefore better termed chloro*iso*-naphthathioxin.

When triturated with concentrated perchloric acid, dehydro-β-naphthol sulphide yields a *perchlorate*, m. p. 128° (decomp.), which is resolved into its components by washing with alcohol.

On oxidation with hydrogen peroxide in acetone solution containing a little glacial acetic acid, *iso*-β-naphthol sulphide is converted into a *meri*quinonoid *compound*, $O{:}C_{10}H_6{:}S{<}\overset{C_{10}H_6}{O}{,}S(C_{10}H_6{\cdot}OH)_2$. This crystallises from a mixture of light petroleum and chloroform in light yellow needles, m. p. 141° (decomp.), containing chloroform (1 mol.), and gives a blue coloration with sulphuric acid; the chloroform may be removed by solution in acetone and precipitation in water. The compound then forms a yellow powder, m. p. 143° (decomp.), containing $1H_2O$. It is reduced by zinc dust and acetic acid to the original *iso*sulphide. When heated at 130—140°, or when dissolved in dilute aqueous sodium hydroxide, it undergoes partial conversion into β-naphthol sulphide and *iso*β-naphtholsulphonium anhydride. The *meri*quinonoid compound cannot be prepared by the direct combination of *iso*-β-naphthol sulphide and *iso*-β-naphtholsulphonium anhydride in

chloroform solution. On further oxidation with hydrogen peroxide in hot glacial acetic acid solution, it yields a *substance*, crystallising with acetic acid in yellow leaflets, m. p. between 70° and 80°. The constitution of the latter substance has not yet been determined, but it is probably a compound of *iso*-β-naphtholsulphonium anhydride with a higher oxidation product.

In agreement with the formula $C_{10}H_6<\begin{matrix}SO_2\\O\cdot O\end{matrix}>C_{10}H_6$, dehydro-β-naphtholsulphone does not react with hydroxylamine nor yield a hydrazone with *p*-nitrophenylhydrazine. It is reduced by hydriodic acid, or by zinc dust and glacial acetic acid, containing a little hydrochloric acid, to a ββ-dinaphthol, which crystallises in elongated leaflets or spherical clusters of slender needles, m. p. 197°, and yields a *diacetyl* derivative in very slender needles, m. p. 113°. This dinaphthol differs from the ordinary ββ-dinaphthol obtained by the direct oxidation of β-naphthol, but is possibly identical with the compound, m. p. 195°, prepared by Kauffmann (A., 1882, 1068) by fusing β-naphtholaldehyde with potassium hydroxide.

On reduction with sodium sulphide or zinc dust and ammonia in boiling methyl alcoholic solution, dehydro-β-naphtholsulphone is transformed into iso-*β-naphtholsulphone*, $SO_2(C_{10}H_6\cdot OH)_2$. This forms a colourless, amorphous powder, which becomes yellow and sinters at 85°, is viscid at 110°, and is completely fused to a mobile liquid at about 125°. It is oxidised by potassium ferricyanide in alkaline solution to the original sulphone, and gives a colourless precipitate with benzenediazonium chloride, thus differing from the isomeric β-naphtholsulphone, which yields 1-benzeneazo-β-naphthol.

When heated either alone at 100° or with acetic acid, formic acid or acetic anhydride, it loses water and forms an *anhydride*, $C_{20}H_{12}SO_3$. The latter compound is converted by boiling acetyl chloride into mono- and di-chloro*iso*naphthathioxin (Nolan and Smiles, T., 1913, **103**, 905). Although the anhydride yields a di-*p*-nitrophenyl hydrazone, its constitution is probably represented by the following formula: $O{:}C_{10}H_6{:}SO<\begin{matrix}C_{10}H_6\\O\end{matrix}$. F. B.

Binuclear Quinones. III. Dianthryl. Alfred Eckert and Alice Hofmann (*Monatsh.*, 1915, **36**, 497—503. Compare Meyer, A., 1909, i, 168; Meyer, Bondy, and Eckert, A., 1913, i, 62).—Dianthryl has been oxidised to dianthranol and the latter reduced to the former. 10 : 10′-*Dihydroxytetrahydrodianthryl* has been obtained as primary product of the reduction of dihydrobianthron; it is isomeric with the anthrapinacone (9 : 9′-dihydroxytetrahydrodianthryl) prepared by Schulze (A., 1886, 248) by the reduction of anthraquinone by zinc dust and ammonia, but distinguished by the greater readiness with which it loses water, yielding dianthryl. The constitutions of these substances are proved by oxidation, since the former gives dihydrodianthrone and the latter anthraquinone.

Dianthryl is conveniently prepared by reducing a solution of anthraquinone in glacial acetic acid with tin and hydrochloric acid in the

presence of a little platinic chloride (compare Liebermann and Gimbl, A., 1887, 965).

Dianthranol acetate is formed by the action of lead peroxide at 50—70° on a suspension of dianthryl in glacial acetic acid, and is saponified by alcoholic potassium hydroxide to dianthranol; concentrated sulphuric acid converts it into dianthrone, oxidation occurring simultaneously with hydrolysis.

Dianthranol is reduced by tin and hydrochloric acid in glacial acetic acid solution in the presence of platinic chloride to dianthryl. Under similar conditions, dihydrodianthrone gives dihydroxytetrahydrodianthryl, yellow needles, m. p. 150—153°. H. W.

Tetrahydroxydiphenyl from the Resorcinol Fusion. Oscar von Friedrichs (*Arkiv. Kem. Min. Geol.*, 1914, **5**, No. 19, 1—20).—The constitution of the tetrahydroxydiphenyl (diresorcinol) obtained to a small extent when resorcinol is fused with sodium hydroxide (Barth and Schreder, A., 1879, 633) is still unsettled, although it is generally assumed that the hydroxyl groups have the position: 3 : 5 : 3′ : 5′ (compare Herzig and Zeisel, A., 1890, 1404; Selch, A., 1893, i, 352; Meyer and Desamari, A., 1909, i, 657; and Benedikt, A., 1880, 246). In order to transform the compound into derivatives of known constitution, the author has investigated the effect of phosphorus tri- and penta-chlorides, but no reaction took place. By oxidation of the tetra-methyl and -ethyl ethers, identifiable products could not be obtained, neither could the compound be obtained by synthesis.

The yield of the tetrahydroxydiphenyl in proportion to that of the phloroglucinol produced at the same time increases with the temperature, indicating that tetrahydroxydiphenyl is a secondary product produced from phloroglucinol; this supports the constitution usually assigned.

The following derivatives have been prepared: Methylation with diazomethane gave the *dimethyl ether*, $C_{12}H_6(OH)_2(OMe)_2,1\frac{1}{2}H_2O$, as colourless leaflets, m. p. 67°; the anhydrous substance has m. p. 76°. The *tetramethyl ether*, $C_{12}H_6(OMe)_4$, is obtained by methylation with either methyl iodide and potassium hydroxide or with dimethyl sulphate. It forms tabular crystals or else white needles, m. p. 108°.

Oxidation of the tetrahydroxydiphenyl with fuming nitric acid gives oxalic acid and a reddish nitro-compound, which is possibly hexanitrotetrahydroxydiphenyl. Styphnic acid is not produced.

Hexa-amino-3 : 5 : 3′ : 5′-*tetrahydroxydiphenyl tetrahydrochloride*, $C_{12}(NH_2)_6(OH)_4,4HCl$,

is obtained as a white, crystalline powder by reduction of the hexanitro-compound (Benedikt and Julius, A., 1884, 1139) with tin and hydrochloric acid. It decomposes at 180—190° without melting. *Hexanitrodiphenyl* 3 : 5 : 3′ : 5′-*tetramethyl ether*, $C_{12}(NO_2)_6(OMe)_4$, obtained from the hexanitro-compound by methylation with diazomethane, forms light yellow needles, m. p. 208°. Nitration of diphenyl-3 : 5 : 3′ : 5′-tetramethyl ether with fuming nitric acid gives *tetranitrodiphenyl* 3 : 5 : 3′ : 5′-*tetramethyl ether*, $C_{12}H_2(NO_2)_4(OMe)_4$, as slender, yellow needles, with no definite melting point. Chlorination of tetrahydroxydiphenyl in carbon disulphide at ordinary temperatures, or in ice-cooled glacial acetic acid, gives *hexachloro*-3 : 5 : 3′ : 5′-

tetrahydroxydiphenyl, $C_{12}(OH)_4Cl_6$, as colourless crystals, m. p. 283°. When the glacial acetic acid is not cooled, *decachloro-3 : 5 : 3′ : 5′-tetrahydroxydiphenyl*, $C_{12}O_4Cl_{10}$, is obtained as slender, white needles, m. p. 170—177°

Hexachloro-3 : 5 : 3′ : 5′-tetrahydroxydiphenyl gives the *tetra-acetyl* compound, $C_{12}Cl_6(OAc)_4$, as colourless needles, m. p. 229°, on acetylation with acetic anhydride and anhydrous sodium acetate. Methylation with diazomethane gives the *dimethyl ether*,

$$C_{12}Cl_6(OH)_2(OMe)_2,$$

m. p. 180°, whilst methyl sulphate gives rise to the *tetramethyl ether*, $C_{12}Cl_6(OMe)_4$, colourless needles, m. p. 220° (sinters at 185°). Under similar conditions, hexabromo-3 : 5 : 3′ : 5′-tetrahydroxydiphenyl (Meyer and Desamari, *loc. cit.*) gives the *hexabromo-dimethyl ether*,

$$C_{12}Br_6(OH)_2(OMe)_2,$$

white crystals, m. p. 194—196°, and the *hexabromo-tetramethyl ether*, $C_{12}Br_6(OMe)_4$, colourless needles, m. p. 211°. *Hexabromodiphenyl 3 : 5 : 3′ : 5′-tetraethyl ether*, $C_{12}Br_6(OEt)_4$, is produced as silky, glistening needles, m. p. 288°, by bromination of the tetraethyl ether in glacial acetic acid. T. S. P.

β-Hydroxy-β-phenylethylamine and Related Compounds. C. MANNICH and E. THIELE (*Arch. Pharm.*, 1915, **253**, 181—195).—The well-known difficulties associated with the reduction of amino-alkyl aryl ketones to the corresponding carbinols have been overcome by the use of hydrogen and palladinised charcoal, and compounds of the type of β-hydroxy-β-phenylethylamine are now rendered available for many interesting syntheses.

Palladinised charcoal is made by passing hydrogen into a suspension of finely powdered animal charcoal, extracted with hydrochloric acid until free from iron, in a solution of palladous chloride, the quantities being arranged so as to give a preparation which contains about 2% of palladium when dried. This catalyst is more suitable than colloidal palladium.

The mixture of the hydrochloride and hydrobromide of ω-aminoacetophenone, as obtained by the action of hexamethylenetetramine on ω-bromoacetophenone (Mannich and Hahn, A., 1911, i, 648), was saturated with hydrogen in the presence of the above catalyst, and the new base was precipitated from the concentrated filtrate as the carbonate, and then converted into the *hydrochloride*, m. p. 211°. The free *β-hydroxy-β-phenylethylamine*, $OH\cdot CHPh\cdot CH_2\cdot NH_2$, was isolated from the alcoholic solution of the salt by adding sodium ethoxide, and was obtained in glistening needles, m. p. about 40°. The base is much more stable than adrenaline towards acids and alkalis. The *N*-benzoyl derivative, m. p. 146° (compare Kolshorn, A., 1904, i, 675), gave a good yield of the *O-acetate*, $OAc\cdot CHPh\cdot CH_2\cdot NHBz$, glistening needles, m. p. 112—113°. Other new *N*-derivatives include: *β-hydroxy-β-phenylethylcarbamide*, $OH\cdot CHPh\cdot CH_2\cdot NH\cdot CO\cdot NH_2$, m. p. 95°, *phenyldichloroacetylaminomethylcarbinol*, $OH\cdot CHPh\cdot CH_2\cdot NH\cdot CO\cdot CHCl_2$, from ethyl dichloroacetate and the free base, glistening leaflets, m. p. 91°, and *phenylcyanoacetylaminomethylcarbinol*,

$$OH\cdot CHPh\cdot CH_2\cdot NH\cdot CO\cdot CH_2\cdot CN,$$

from ethyl cyanoacetate, m. p. 111°. With ethyl chloroacetate, however, the condensation took place at the chlorine atom and then proceeded to the formation of 3 : 6-*diketo*-1 : 4-*di*-*β*-*hydroxy*-*β*-*phenylethylpiperazine*, $OH\cdot CHPh\cdot CH_2\cdot N<\begin{matrix}CH_2\cdot CO\\CO\cdot CH_2\end{matrix}>N\cdot CH_2\cdot CHPh\cdot OH$, m. p. 121°.

A concentrated solution of ω-amino-*p*-methoxyacetophenone was also reduced to *β*-hydroxy-*β*-*p*-methoxyphenylethylamine hydrochloride (Rosenmund, A., 1913, i, 465), which yielded the N-*benzoyl* derivative, m. p. 151—152°, and this gave p-*methoxyphenylbenzoylaminomethylcarbinyl acetate*, $OMe\cdot C_6H_4\cdot CH(OAc)\cdot CH_2\cdot NHBz$, m. p. 139°. p-*Methoxyphenylcarbethoxyaminomethylcarbinol*,

$$OMe\cdot C_6H_4\cdot CH(OH)\cdot CH_2\cdot NH\cdot CO_2Et,$$

forms leaflets, m. p. 95°, and *β*-*hydroxy*-p-*methoxyphenylethylcarbamide*,

$$OMe\cdot C_6H_4\cdot CH(OH)\cdot CH_2\cdot NH\cdot CO\cdot NH_2,$$

has m. p. 122—123°.

ω-Amino-*p*-hydroxyacetophenone hydrochloride, obtained by the action of hydriodic acid on the above methoxy-compound (compare Mannich and Hahn, *loc. cit.*), was reduced to *β*-*hydroxy*-*β*-p-*hydroxyphenylethylamine hydrochloride*, m. p. 172° (decomp.), free *base*, m. p. 157—158°, which yielded the *dibenzoyl* derivative,

$$OBz\cdot C_6H_4\cdot CH(OH)\cdot CH_2\cdot NHBz,$$

m. p. 215°, by the Schotten-Baumann method, and this gave the O-*acetate*, $C_{24}H_{21}O_5N$, hard granules, m. p. 170°, when boiled with acetic anhydride. J. C. W.

Preparation of Hydroxy-derivatives of Aliphatic Aromatic Ethers. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 282991; from *J. Soc. Chem. Ind.*, 1915, **34**, 735).—The products obtained by treating homologues of ethylene glycol with phenols, their homologues, or substitution products are more powerful analgesics than the ethylene glycol aryl ethers. They have the general formula $HO\cdot CHR^1\cdot CHR^2\cdot OR$, where R is an aryl radicle, whilst as regards R^1 and R^2 one is hydrogen, the other an alkyl group. *Propyleneglycol phenyl ether*, $OH\cdot CH_2\cdot CHMe\cdot OPh$, is described. G. F. M.

Preparation of Aromatic Carboxylic Acids Chlorinated in the Nucleus. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 282133; from *J. Soc. Chem. Ind.*, 1915, **34**, 652).—Aromatic sulphonic acids containing methyl groups in the ring when heated above 200° with thionyl chloride with or without an indifferent solvent are converted according to the temperature into mono-, di-, or tri-chloro-derivatives which form acids on heating with water, alkalis, or acids. Thus *o*- or *p*-toluenesulphonic acids yield *o*- or *p*-chlorobenzoic acids in a high state of purity. G. F. M.

Action of Light on Benzophenone and Butyric Acid. R. DE FAZI (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 942—945. Compare Paternò, this vol., i, 493).—Further investigation of the products

yielded by this reaction shows that the latter proceeds in two distinct directions, (1) with formation of propyl butyrate and, consequently, of carbon dioxide and benzopinacone, and (2) with synthesis of an acid by addition of 1 mol. of benzophenone to 1 mol. of butyric acid. This *acid*, $C_{17}H_{18}O_3$, forms ill-defined, brick-yellow crystals, m. p. 125—130°; its *silver* salt was prepared. It may be either β-hydroxy-ββ-diphenyl-α-ethylpropionic acid, δ-hydroxy-δδ-diphenylvaleric acid, or, most probably, γ-hydroxy-γγ-diphenyl-β-methylbutyric acid,

$$OH\cdot CPh_2\cdot CHMe\cdot CH_2\cdot CO_2H$$

(compare Paternò & Chieffi, A., 1911, i, 65). T. H. P.

Racemisation of Phenyl-*p*-tolylacetic Acid. ALEX. MCKENZIE and SIBYL TAITE WIDDOWS (T., 1915, **107**, 702—715).—Since the racemisation phenomena already described in connexion with mandelic acid (T., 1904, **85**, 378, 1249) may possibly be due to the presence of both a hydroxyl and hydrogen atom, in direct union with the asymmetric carbon atom, an examination has been made of the behaviour of phenyl-*p*-tolylacetic acid, in which the hydroxyl group of mandelic acid is substituted by a hydrocarbon residue. The results obtained show, however, that optically active phenyl-*p*-tolylacetic acid is even more readily racemised than is mandelic acid under similar conditions. Not only is the active acid partly racemised by boiling with aqueous potassium hydroxide, but in the form of its *l*-menthyl and *l*-bornyl esters undergoes profound racemisation during saponification with alkalis, the resulting acid being either inactive or only very slightly active.

It is particularly noteworthy that the ester recovered after fractional hydrolysis of *l*-menthyl *d*-phenyl-*p*-tolylacetate by alkalis was partly racemised, indicating that the ester itself undergoes catalytic racemisation prior to saponification.

Complete racemisation was found to occur during the saponification of the ethyl *d*-ester with alcoholic potassium hydroxide, and also when the *d*-acid chloride was submitted to the Friedel-Crafts' reaction with benzene and aluminium chloride.

After reviewing the literature dealing with the racemisation of acids, the authors express the opinion that the most satisfactory explanation hitherto advanced to account for the catalytic racemisation of optically active acids, having the asymmetric carbon atom in the α-position, is that based on the assumption of a desmotropic change, thus: $CHRR'\cdot CO_2H \longrightarrow CRR':C(OH)_2$.

In view, however, of the reactivity of the carbonyl group and the absence of any definite evidence, either chemical or physical, of the existence in solution of dihydroxy-compounds of the above type, it is suggested that an additive compound of the acid with the catalyst is first formed, and it is this unstable compound and not the free acid itself which undergoes desmotropic change, as illustrated in the following scheme:

$$CHRR'\cdot CO_2H \longrightarrow CHRR'\cdot C(OH):O<^{K}_{OH} \longrightarrow$$

$$CRR':C(OH)\cdot OH<^{K}_{OH} \longrightarrow CHRR'\cdot CO_2K + H_2O.$$

The resolution of *r*-phenyl-*p*-tolylacetic acid was accomplished by crystallisation of its cinchonidine salt from alcohol, the salt of the *d*-acid being the more sparingly soluble. The *l*-acid, obtained by crystallising the quinine salt of the acid recovered from the mother liquors, is difficult to isolate in a pure condition, probably on account of the formation of mixed crystals of the quinine salts of the enantiomorphously related acids.

The *r*-acid may also be slightly activated by fractional esterification with *l*-menthol, the *l*-acid being esterified more rapidly than the *d*-isomeride.

d-*Phenyl*-p-*tolylacetic acid* crystallises in feathery needles, m. p. 83—84° with slight preliminary softening, $[\alpha]_D^{19\cdot4} + 14\cdot6°$ in acetone; *ethyl* ester, feathery needles, m. p. 39—40°, $[\alpha]_D^{15} + 10\cdot4°$ in acetone; *cinchonidine* salt, needles, m. p. 204—205° (decomp.), $[\alpha]_D^{16} - 35°$ in chloroform. l-*Phenyl*-p-*tolylacetic acid* has $[\alpha]_D - 13\cdot9°$ in acetone.

The following esters were prepared by the interaction of the corresponding acid chlorides with *l*-menthol and *l*-borneol in the presence of benzene and pyridine: l-*menthyl* r-*phenyl*-p-*tolylacetate*, rectangular crystals, m. p. 54—55°, b. p. 250°/12 mm., $[\alpha]_D^{15\cdot6} - 59\cdot2°$ in acetone; l-*menthyl* d-*phenyl*-p-*tolylacetate*, feathery needles, m. p. 53—54°, $[\alpha]_D^{14} - 53\cdot0°$; l-*menthyl* l-*phenyl*-p-*tolylacetate*, m. p. 57—58°; l-*bornyl* r-*phenyl*-p-*tolylacetate*, an oil having a bright blue colour when freshly distilled, b. p. 249°/12 mm.; l-*bornyl* d-*phenyl*-p-*tolylacetate*, b. p. 240°/13 mm.

r-*Phenyl*-p-*tolylacetophenone*, obtained by the interaction of both the *r*- and *d*-acid chlorides with benzene in the presence of aluminium chloride, forms hexagonal plates, m. p. 159—160°. F. B.

Preparation of the Hexamethylenetetramine Salt of the ω-Methylsulphonate of *p*-Aminophenyl Salicylate. J. Abelin, E. Bürgi, and M. Perelstein (D.R.-P. 282412; from *J. Soc. Chem. Ind.*, 1915, **34**, 686).—Hexamethylenetetramine combines with the ω-methylsulphonate of *p*-aminophenyl salicylate to form a compound, $C_{20}H_{25}O_6N_5S$, which combines the therapeutic properties of a salol derivative with those of hexamethylenetetramine. It acts as an anæsthetic without any unpleasant subsidiary effects. G. F. M.

Esters of Carboxyarylphosphoric Acids. Synthetic Patents Co., New York (U.S. Pat. 1125081; from *J. Soc. Chem. Ind.*, 1915, **34**, 451).—Esters of the type, $RO_2C\cdot Aryl\cdot O\cdot PO(OH)_2$, are prepared by treating aromatic hydroxy-acids with phosphorus haloids and then condensing the halogenocarboxyarylphosphoric acid haloids with an alcohol, phenol, phenol-alcohol, or hydroxy-acid. They are colourless, crystalline products which form soluble salts, and are said to be efficacious against infectious diseases.

The *guaiacol* ester of p-*carboxyphenylphosphoric acid*,

$$OMe\cdot C_6H_4\cdot O\cdot CO\cdot C_6H_4\cdot O\cdot PO(OH)_2,$$

has m. p. 182°, and is especially mentioned. The m-*tolyl* ester, m. p. 179°, and the *thymol* ester, m. p. 163°, of the same acid are other examples. J. C. W.

Diacetylcatechol-*o*-carboxylic [2 : 3-Diacetoxybenzoic] Acid Compound. SYNTHETIC PATENTS CO., NEW YORK (U.S. Pat. 1140716; from *J. Soc. Chem. Ind.*, 1915, **34**, 734).—Acetylated catechol-*o*-carboxylic acid derivatives are claimed as antipyretics, particularly the diacetyl compound of the probable formula $C_6H_3(OAc)_2 \cdot CO_2H$ (1 : 2 : 3), a white powder, soluble in the usual organic solvents, insoluble in water, and melting at 148—150°. G. F. M.

Preparation of Unsaturated Acids of the Anthraquinone Series. FARBENFABRIK VORM. F. BAYER & CO. (D.R.-P. 282265; from *J. Soc. Chem. Ind.*, 1915, **34**, 652).—Anthraquinone-2-aldehyde or a ω-dihalogen-2-methylanthraquinone condenses with an acetate to form anthraquinonyl-2-acrylic acid. G. F. M.

Ethyl Hydrogen Phthalate. WALTER VON AMANN (*Monatsh.*, 1915, **36**, 505—508).—Ethyl hydrogen phthalate has been previously described only in the liquid form. By the interaction of ethyl alcohol and phthalic anhydride, in a special apparatus arranged so as to completely exclude moisture, the author has prepared it in well-defined monoclinic crystals [$a : b : c = 0{\cdot}6425 : 1 : 0{\cdot}5197$; β 91°2′], m. p. 47—48°. It is very readily saponified by alkalis, and cannot be accurately titrated with sodium hydroxide solution. H. W.

Formation and Stability of *spiro*-Compounds. I. *spiro*-Compounds from *cyclo*Hexane. R. M. BEESLEY, C. K. INGOLD, and J. F. THORPE (T., 1915, **107**, 1080—1106).—An investigation has been commenced of the effect produced by the alteration of the tetrahedral angle, owing to ring formation, on the formation and stability of a second ring joined to the first by a common quaternary carbon atom, and the results indicate that ring formation under these circumstances occurs with greater facility than with a corresponding compound having an open-chain structure. This is held to indicate that the bending outwards of the two valencies participating in the original ring (to 120° in the case of a *cyclo*hexane derivative) causes the other valencies to distribute themselves equally in the remaining space. They become placed therefore closer together than the normal 109°28′ in the open-chain compound, and hence the greater facility for the formation of a second ring. The experiments have been carried out with bromo-derivatives of *cyclo*hexane-1 : 1-diacetic acid, the behaviour of which with alcoholic potassium hydroxide, etc., was compared with that of ethyl dibromodimethylglutarate. Bromination of *cyclo*hexane-1 : 1-diacetic acid gave rise to *ethyl αα′-dibromo*cyclo*hexane*-1 : 1-*diacetate* in both *cis*- and *trans*-forms, and to the corresponding *trans*-monobromolactone. The dibromo-compounds could not be isolated in a pure condition, but the lactones, which are also formed by distillation of the dibromo-compounds in vacuum, were obtained analytically pure. trans-*Lactone* of *ethyl α-bromo-α′-hydroxy*-cyclo*hexane*-1 : 1-*diacetate* forms prisms, m. p. 96°, b. p. 225—230°/20 mm. The cis-*lactone* forms needles, m. p. 69—70°. An acid product of the bromination was also isolated. It consisted mainly of the acid monobromo-ester, as on treatment with sodium carbonate it gave the *lactone* of *α-hydroxy*cyclo*hexane*-1 : 1-*diacetic acid*, small needles, m. p.

91—92°. The corresponding acid was stable only in the form of its salts. An *aniline* salt, m. p. 104°, and a *dianilide*, m. p. 97°, of this hydroxy-acid were obtained. trans-cyclo*Hexane*-spiro-cyclo*propane*-1 : 2-*dicarboxylic acid*, $C_5H_{10}>C<\begin{matrix}CH\cdot CO_2H\\CH\cdot CO_2H'\end{matrix}$ was obtained by the action of concentrated potassium hydroxide at 150° on the above acid monobromo-ester. It forms flat needles, m. p. 237°, and gives a dianilide, m. p. 292°. The corresponding cis-cyclo*hexane*-spiro-cyclo*propane*-1 : 2-*dicarboxylic acid* was obtained from the filtrate from the *trans*-acid, and also by distilling the latter under ordinary pressure. It is thus obtained as its *anhydride*, $C_5H_{10}>C<\begin{matrix}CH\cdot CO\\CH\cdot CO\end{matrix}>O$, m. p. 102°, from which the acid itself is formed in the usual way. It forms needles, m. p. 198°. The *anilic acid* melts at 207° (decomp.), and the *anil* at 119°.

The action of alkalis on the bromo-lactone esters gives rise to a variety of products according to conditions. *cyclo*Hexylideneacetic acid, $C_5H_{10}>C:CH\cdot CO_2H$, m. p. 92°, was formed by the action of 10% aqueous sodium hydroxide on either of the bromo-lactones (m. p. 96° or 70°). By the action of 64% aqueous potassium hydroxide this acid was converted into Δ^1-*cyclo*hexeneacetic acid, m. p. 38°, and the latter is therefore among the products of the action of this reagent on the bromo-lactones. The trans- and cis-*lactonic acids* of *aa' dihydroxy*cyclo*hexane*-1 : 1-*diacetic acid* were obtained by the action of 15 or 64% potassium hydroxide on the *trans*- and *cis*-bromolactones, and were isolated as their esters from the other products of the reaction. Hydrolysis with hydrochloric acid gave the *trans*-lactonic acid, m. p. 145°, forming a *dianilide*, m. p. 169°, and the *cis*-lactonic acid, m. p. 168°, forming a *dianilide*, m. p. 169°. cyclo*Hexane*-spiro-cyclo*propanol*-2 : 3-*dicarboxylic acid*, $C_5H_{10}>C<\begin{matrix}C(OH)\cdot CO_2H\\CH\cdot CO_2H\end{matrix}$, was obtained in 27% yield from the *trans*-bromolactone by the action of boiling 64% potassium hydroxide. It forms colourless, pearly plates, m. p. 217°, and gives a *dianilide*, m. p. 202°. The acid is very stable to acid permanganate, phosphorus pentachloride, and acetyl chloride. By the action of concentrated sulphuric acid it yields a small quantity of cyclo*hexane*-spiro-cyclo*propanone*, $C_5H_{10}>C<\begin{matrix}CH_2\\CO\end{matrix}$, which gives a *semi-carbazone*, m. p. 175°. On heating with water in a sealed tube, the hydroxy-*spiro*-acid underwent fission with formation of the lactonic acid of *a-hydroxy-a'*-cyclo*hexan*-1-*olsuccinic acid*,

$$C_5H_{10}>C<\begin{matrix}O\text{————}CO\\CH(CO_2H)\cdot CH\cdot OH'\end{matrix}$$

cubical prisms, m. p. 131°. The disodium, disilver, and monobasic aniline salts are described. The latter melts at 123°. G. F. M.

2-Hydroxy-3-methoxybenzaldehyde. E. Rupp and K. Linck (*Arch. Pharm.*, 1915, **253**, 33—41).—This aldehyde, pale greenish-yellow, long, ciliated needles, m. p. 44—45°, is a by-product in the technical preparation of vanillin from guaiacol, and is recommended as

a dye for animal fibres (D.R.-P. 272736). A number of derivatives are now described.

The *oxime*, $OMe{\cdot}C_6H_3(OH){\cdot}CH{:}NOH$, forms colourless, slender needles, m. p. 121°; the *azine*, $C_{16}H_{16}O_4N_2$, crystallises in slender, yellow needles, m. p. 196°; the *anil*, $OMe{\cdot}C_6H_3(OH){\cdot}CH{:}NPh$, orange needles, has m. p. 84°; the *phenylhydrazone*, $C_{14}H_{14}O_2N_2$, forms felted needles, m. p. 128°.

2 : 3-*Dimethoxybenzaldehyde*, $C_9H_{10}O_3$, prepared by the action of methyl sulphate, has m. p. 54—55°; 2-*benzoyloxy*-3-*methoxybenzaldehyde*, $OMe{\cdot}C_6H_3(OBz){\cdot}CHO$, has m. p. 90°; 2-*benzenesulphoxy*-3-*methoxybenzaldehyde*, $CHO{\cdot}C_6H_3(OMe){\cdot}O{\cdot}SO_2Ph$, forms glistening leaflets, m. p. 121°. The latter derivative is easily prepared and easily hydrolysed, so that it is useful in reactions in which the hydroxyl group must be rendered dormant. The product of the action of acetic anhydride and a few drops of sulphuric acid, namely, 2-*acetoxy*-3-*methoxybenzylidene diacetate*, $OMe{\cdot}C_6H_3(OAc){\cdot}CH(OAc)_2$, forms pale yellow crystals, m. p. 83°.

5-*Nitro*-2-*hydroxy*-3-*methoxybenzaldehyde*, $C_8H_7O_5N$, prepared by adding the required amount of nitric acid (D 1·4) to the cold solution in glacial acetic acid, forms pale yellow needles, m. p. 142°. 5-*Bromo*-2-*hydroxy*-3-*methoxybenzaldehyde*, $C_8H_7O_3Br$, is a glistening, yellow compound, m. p. 127°.

The aldehyde is comparatively stable, and could not be oxidised without involving the hydroxyl group. The above benzenesulphonyl derivative, however, when mixed with magnesium sulphate solution and treated with the required volume of 3% permanganate on the water-bath, yielded 2-*benzenesulphoxy*-3-*methoxybenzoic acid*, m. p. 195°. This was hydrolysed by warm 3% sodium hydroxide to 2-*hydroxy*-3-*methoxybenzoic acid*, $C_8H_8O_4$, which crystallises in colourless leaflets, m. p. 148°, and forms a *silver* salt and a *methyl* ester, m. p. 67—68° with a faint aromatic odour. The latter acid is formed quantitatively by the alkali fusion at 215°. At about 250°, a quantitative yield of catechol-*o*-carboxylic acid is obtained, which proves the constitution of the aldehyde.

When heated with acetic anhydride and sodium acetate at 180—200°, the chief product is the *lactone* of β-2-*hydroxy*-3-*methoxyphenylacrylic acid* [5-*methoxycoumarin*], $OMe{\cdot}C_6H_3\langle^{CH:CH}_{O---CO}$, which forms silky needles, m. p. 89°. The reduction product of this, namely, 5-*methoxy*-3 : 4-*dihydrocoumarin*, $C_{10}H_{10}O_3$, has m. p. 107°, and the corresponding *dibromide* (β-2-*hydroxy*-3-*methoxyphenyl*-αβ-*dibromopropiolactone*) has m. p. 165°. J. C. W.

1 : 3-Dimethyl*cyclo*hexan-2-one and 1 : 2 : 3-Trimethyl-Δ^1-*cyclo*hexene. K. VON AUWERS and F. KROLLPFEIFFER (*Ber.*, 1915, **48**, 1226—1233).—The method of Haller (A., 1913, i, 984) for the preparation of 1 : 3-dimethyl*cyclo*hexan-2-one by the action of sodium amide and methyl iodide on 1-methyl*cyclo*hexan-2-one is not satisfactory, the yield being poorer than stated; also the process of purification treatment with benzaldehyde is stated to be futile.

1 : 3-Dimethyl*cyclo*hexan-2-one was prepared by the action of

hydrogen and palladium on 1-methyl-3-hydroxymethylene*cyclo*hexan-2-one (Kötz and Schaeffer, A., 1912, i, 603; 1914, i, 186); the product, b. p. 53·6—55·3°/10 mm., D_4^{20} 0·914, n_D^{20} 1·4482, was converted by successive treatment with magnesium methyl iodide and anhydrous oxalic acid into 1 : 2 : 3-*trimethyl*-Δ^1-cyclo*hexene*,

$$CMe\begin{matrix}\diagup CMe\text{——}CH_2\diagdown \\ \diagdown CHMe\text{—}CH_2\diagup\end{matrix}CH_2,$$

a colourless, mobile liquid, b. p. 149·6—150°/749 mm., D_4^{20} 0·828, n_D^{20} 1·4593, which was analysed as the *nitrosochloride*, a blue oil.

D. F. T.

Quaternary Salts of Hexamethylenetetramine. VII. ω-Halogen Derivatives of Aliphatic-Aromatic Ketones and their Hexamethylenetetraminium Salts. Walter A. Jacobs and Michael Heidelberger (*J. Biol. Chem.*, 1915, **21**, 455—464).—The work described in the preceding papers has been extended to derivatives of ω-bromo- and ω-iodo-acetophenone.

The additive *compound* of ω-bromoacetophenoneoxime and hexamethylenetetramine, $C_{14}H_{20}ON_5Br$, has m. p. 139° (decomp.).

p-Tolyl bromomethyl ketone yields a hexamethylenetetramine *compound*, crystallising in slightly pinkish, minute prisms, m. p. 148—149°, and reacts with sodium iodide in acetone solution at the ordinary temperature to form p-*tolyl iodomethyl ketone*, $C_6H_4Me\cdot CO\cdot CH_2I$, cream-coloured needles, m. p. 42—43° (corr.), which yields a hexamethylenetetramine *compound*, crystallising in colourless, micro-needles, melting at 157—158° to a reddish-brown tar.

4-o-*Xylyl bromomethyl ketone*, $C_6H_3Me_2\cdot CO\cdot CH_2Br$, prepared from *o*-xylene, bromoacetyl bromide and aluminium chloride in carbon disulphide solution, forms large, slightly brown needles, m. p. 62—62·5° (corr.), and is probably identical with the substance, m. p. 63—64°, obtained by Armstrong and Kipping (T., 1893, **63**, 86) by brominating *o*-xylyl methyl ketone; the hexamethylenetetramine *compound* melts at 137—138° to a red liquid.

4-m-*Xylyl bromoethyl ketone*, prepared in a similar manner, forms colourless micro-leaflets of an irritating odour, m. p. 42—43° (corr.), and yields a hexamethylenetetramine *compound*, crystallising in rosettes of needles, m. p. 145—146° (decomp.).

p-*Ethylphenyl bromomethyl ketone*, from ethyl benzene and bromoacetyl bromide, forms glistening micro-platelets, m. p. 33—34° (corr.) with slight preliminary softening, and yields a hexamethylenetetramine *compound* in minute, glistening prisms, m. p. 146—147° (decomp.).

2 : 4 : 6-*Trimethylphenyl bromomethyl ketone*, prepared from mesitylene in a similar manner, crystallises in colourless, glistening plates, m. p. 55—56° (corr.).

The additive *compound* of ω-bromo-*m*-nitroacetophenone and hexamethylenetetramine has m. p. 157° (decomp.).

p-*Acetylaminophenyl bromomethyl ketone*, $NHAc\cdot C_6H_4\cdot CO\cdot CH_2Br$, from acetanilide and bromoacetyl bromide in the presence of aluminium chloride, forms cream-coloured prisms, m. p. 190—193° (decomp.), and yields a hexamethylenetetramine *compound*, cream-coloured prisms, m. p. 194° (decomp.).

The additive *compound* of *p*-aminophenyl chloromethyl ketone and hexamethylenetetramine forms light yellow micro-crystals.

3-*Acetylamino*-p-*tolyl bromomethyl ketone*, $NHAc\cdot C_6H_3Me\cdot CO\cdot CH_2Br$, from aceto-*o*-toluidide and bromoacetyl bromide, crystallises in drab, felted needles, m. p. 167—170° with preliminary softening, and yields a hexamethylenetetramine *compound*, as a pale brown, micro-crystalline powder (decomp. 150—155°).

3-*Acetylamino*-p-*tolyl β-iodoethyl ketone*,

$$NHAc\cdot C_6H_3Me\cdot CO\cdot CH_2\cdot CH_2I,$$

from aceto-*o*-toluidide and *β*-iodopropionyl chloride, crystallises in faintly green, felted needles, m. p. 142—143° (corr. decomp.), and forms a hexamethylenetetramine *compound*, which becomes yellow at about 150°, m. p. 161—162° (decomp.): the position of the substituting groups has been established by the formation of 3-acetylamino-*p*-toluic acid, m. p. 279—281° (corr.), on oxidation with potassium permanganate in acetone solution.

The additive *compound* of *p*-methoxyphenyl bromomethyl ketone and hexamethylenetetramine forms faintly yellow micro-crystals, m. p. 172° (decomp.); that of *p*-ethoxyphenyl bromomethyl ketone, slightly yellow micro-prisms, m. p. 159—159·5° (decomp.).

3-*Bromoacetyl*-2-*methylquinoline*, $C_6H_4\langle\begin{matrix}CH:C\cdot CO\cdot CH_2Br\\ |\\ N=CMe\end{matrix}$, prepared by brominating 3-acetylquinaldine in strong hydrobromic acid solution (D 1·49) at 50°, crystallises in almost colourless rhombs, m. p. 102—103° (corr.) with slight preliminary softening and slowly decomposes when heated above 50°; the hexamethylenetetramine *compound* has m. p. above 170° (decomp.). F. B.

A New Synthesis of Aromatic Ketones. I. Preparation of Some Phenolic Ketones. KURT HOESCH (*Ber.*, 1915, **48**, 1122—1133).—The limitations of the Friedel-Crafts and the Nencki methods for the synthesis of phenolic ketones render desirable the discovery of other methods, which may supply compounds which cannot be produced by these two well-known processes. A new method for the formation of phenolic ketones has now been discovered in a modification of Gattermann's method for the preparation of phenolic aldehydes from a phenol, hydrocyanic acid and hydrogen chloride, and has been applied to the preparation of compounds hitherto accessible only with difficulty. The method is to take an equimolecular mixture of a phenol and a nitrite in ethereal solution, with the addition of zinc chloride if necessary, and to pass in hydrogen chloride. A ketone-imide hydrochloride of the type $CRR':NH,HCl$ is produced, and this on treatment with water undergoes hydrolysis to the corresponding ketone.

[WITH M. SCHULZE.]—If a mixture of resorcinol and acetonitrile in ethereal solution in the presence of zinc chloride is treated with hydrogen chloride, the ketone-imide hydrochloride begins to separate in half-an-hour, and treatment of this product with water converts it into resacetophenone, m. p. 144—145°, the yield being 70% of the theoretical. The monomethyl ether of resorcinol under analogous treatment gives paeonol (6-hydroxy-4-methoxyacetophenone) together with iso*paeonol*

(*4-hydroxy-2-methoxyacetophenone*), needles, m. p. 138°, which unlike its isomeride shows no colour reaction with ferric chloride.

Anhydrous orcinol, when submitted to this process, was converted into *orcacetophenone* [*3 : 5-dihydroxy-o-tolyl methyl ketone*], silky needles, m. p. 159°. In this case the *sulphate* of the intermediate ketone-imide can be isolated without difficulty, and forms colourless needles which readily decompose when boiled with water, giving the above phenolic ketone. Under similar conditions to those in the preceding cases, the monomethyl ether of resorcinol is converted into *aceto-evernone* [*3-hydroxy-5-methoxy-o-tolyl methyl ketone*], quadratic tablets, m. p. 150°, and iso*acetoevernone* [*5-hydroxy-3-methoxy-o-tolyl methyl ketone*]. The *sulphate* of the intermediate ketone-imide was isolated in the form of colourless needles.

By submitting phloroglucinol to this reaction with acetonitrile and hydrogen chloride, phloracetophenone, m. p. 218°, was obtained, probably identical with the aceto*cyclo*hexantrione of Heller (A., 1912, i, 274; also Leuchs and Sperling, this vol., i, 141).

Acetonitrile can be replaced in this synthetical process by benzonitrile and condensation of resorcinol with this compound produces benzoresorcinol, m. p. 144°, whilst orcinol in a similar manner gives rise to *benzo-orcinol* [*phenyl 3 : 5-dihydroxy-o-tolyl ketone*], tablets, m. p. 141°, which shows a reddish-brown colour reaction with ferric chloride. The *hydrochloride* of the intermediate ketone-imide is stable in acid solution and crystallises in yellow needles. *Benzophloroglucinol* [*2 : 4 : 6-trihydroxybenzophenone*], $C_6H_2Bz(OH)_3$, was obtained in an analogous manner from benzonitrile and phloroglucinol; it forms needle crystals, m. p. 165°, and gives a brownish-red coloration with ferric chloride; the intermediate ketone-imide was isolated in the form of its *sulphate*, yellow prisms. D. F. T.

The Constitution of the 4 : 4′-Dichlorodinitro- and 4 : 4′-Dibromodinitro-benzophenones obtained by Nitration of 4 : 4′-Dichloro- and 4 : 4′-Dibromo-benzophenones. P. J. Montagne (*Ber.*, 1914, **48**, 1027—1037).—The nitro-groups present in the 4 : 4′-dichlorodinitro- and 4 : 4′-dibromodinitro-benzophenones obtained by nitration of 4 : 4′-dichloro- and 4 : 4′-dibromobenzophenones must occupy similar positions, because both compounds yield the same dinitrodiaminobenzophenone when treated with ammonia. The actual position of the nitro-groups was determined by reduction of the dibromodinitro-compound with sodium amalgam and alcohol to 3 : 3′-diaminobenzhydrol, the identity of this substance being confirmed by a comparison with the reduction product of 3 : 3′-dinitrobenzophenone. The above compounds are therefore 4 : 4′-dibromo- and 4 : 4′-dichloro-3 : 3′-dinitrobenzophenones.

4 : 4′-Dibromo-3-nitrobenzophenone, b. p. 287°/10 mm., m. p. 119·5°, crystallises in monoclinic tablets [$a : b : c = 2·6352 : 1 : 4·4498$, $\beta = 89·18°$]; it was prepared by condensation of 4-bromo-3-nitrobenzoyl chloride and bromobenzene at 80—90° in the presence of aluminium chloride. 4 : 4′-Dibromo-3 : 3′-dinitrobenzophenone, m. p. 157·5°, prepared by nitration of the preceding compound and also of 4 : 4′-dibromobenzophenone, was converted by reduction with stannous

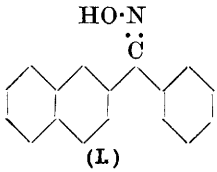
chloride and hydrochloric acid into 4 : 4′-dibromo-3 : 3′-diaminobenzophenone, m. p. 178·5—179°, and by alcoholic ammonia solution at 150° for two days into 3 : 3′-dinitro-4 : 4′-diaminobenzophenone, m. p. 293·5°. The last compound was also obtained in like manner from 4 : 4′-dichloro-3 : 3′-dinitrobenzophenone, and treatment of the chloro- and bromo-compounds with aniline in alcoholic solution at 150° yielded the same 3 : 3′-dinitro-4 : 4′-dianilinobenzophenone, m. p. 226·5°. Reduction of the dinitrodiaminobenzophenone produced 3 : 4 : 3′ : 4′-tetra-aminobenzophenone, yellow needles, m. p. 217°, which as an ortho-diamine condenses with phenanthraquinone in acetic acid solution, giving a diphenanthraphenazine ketone, m. p. 370—380°.

The above results as to m. p.'s of the various substances deviate considerably from those previously recorded by Consonno (A., 1904, i, 676), the discrepances being more than 160° in the case of 3 : 3′-dinitro-4 : 4′-diaminobenzophenone. The cause of the discrepancy is not clear, because Consonno arrives at a similar conclusion as to the constitution of his product. The author's views as to the identity of the compounds mentioned above receive support from the results of Maron and Fox (this vol., i, 266), who record a m. p. 287—289° for 3 : 3′-dinitro-4 : 4′-diaminobenzophenone.

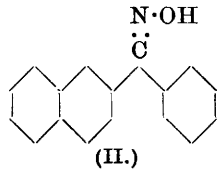
D. F. T.

Stereoisomeric Oximes of Phenyl β-Naphthyl Ketone. Pasquale Poccianti (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 1135—1137).—Betti and Poccianti (A., 1914, i, 550) have shown that phenyl α-naphthyl ketone forms two stereoisomeric oximes, and the author now finds that the same is the case with phenyl β-naphthyl ketone, the two oximes crystallising (1) in small, regular octahedra, m. p. 157°, and (2) in tufts of long, silky needles, m. p. 174° (compare Kegel, A., 1888, 1307). Perrier and Caille's so-called oxime, m. p. 133° (A., 1908, i, 656), appears to be a mixture of the two stereoisomeric oximes with unaltered ketone. Hydroxylamine acts more readily on phenyl β-naphthyl ketone than on phenyl α-naphthyl ketone, owing to the absence in the former case of the steric hindrance exerted by the second nucleus of the naphthalene molecule.

When subjected to the Beckmann rearrangement by treatment with phosphorus pentachloride, oxime (I) yields the β-naphthalide of benzoic acid and oxime (II) the anilide of β-naphthoic acid, so that the structures of the two oximes may be represented thus :



(I.)



(II.)

Reduction of these oximes is difficult and yields the oily *base*,

$$C_{10}H_7\cdot CHPh\cdot NH_2,$$

which readily absorbs carbon dioxide from the air; its *hydrochloride*, m. p. 265—270° (decomp.), *acetate*, m. p. 127°, and *benzoyl* derivative, m. p. 182°, were analysed.

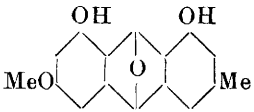
T. H. P.

Commercial Chrysarobin. Robert Eder (*Arch. Pharm.*, 1915, **253**, 1—33).—The identification of the constituents of chrysarobin is particularly difficult because many of them are easily oxidisable substances. Before investigating the drug itself the author has therefore thought it advisable to study the oxidation products of chrysarobin, and has obtained results which, when referred back to the original mixture, agree, in the main, with those of Tutin and Clewer (T., 1912, **101**, 290).

A current of air was passed into a suspension of chrysarobin in 1% sodium hydroxide, whereby the major portion dissolved and hydrogen peroxide was produced (compare Manchot, A., 1901, ii, 93). The red solution was acidified with sulphuric acid when a large quantity of a brown powder separated. The pale yellow acid filtrate was shaken with benzene, which dissolved a very small amount of emodin. The brown powder was ground with 10% sodium carbonate and evaporated to dryness, and the violet residue was exhausted with hot benzene. The insoluble part was considerable and gave brown products on acidifying, but nothing definite could be isolated from it. It is considered that the hydrogen peroxide may be responsible for the production of these by-products. The benzene solution was shaken with 10% sodium carbonate, which dissolved emodin. This was obtained in orange-red needles, m. p. 256—257°, by sublimation at 225°/12 mm., and was converted into the triacetate, m. p. 197°.

The remaining benzene solution contained chrysophanic acid and emodin monomethyl ether, and considerable attention was given to the separation of these. From a Zeisel estimation, it appeared that the mixture contained about 71% of the acid to 29% of the ether. About one-third of the ether could be isolated in a pure state by boiling the mixture with much alcohol, in which it is less soluble than chrysophanic acid, but the latter could not be purified in this way. Sublimation in a vacuum was without avail. The pure acid could be obtained, however, by converting the ether by demethylation into emodin, and extracting this with sodium carbonate. This could be done by hydriodic acid, but the reducing action of this agent necessitated the re-oxidation of the product. Hydrobromic acid and aluminium chloride were also found to be unsuitable agents. Success was attained, however, by using hydrochloric acid at 190° (Fischer and Gross, A., 1911, i, 866), or concentrated sulphuric acid at 160° (Oesterle and Johann, A., 1910, i, 860).

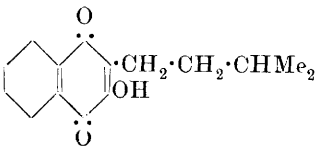
The part of the oxidation product which remained undissolved in the sodium hydroxide was also evaporated with sodium carbonate and then extracted with benzene. The chief constituent of the solution was dehydroemodinanthranol monomethyl ether (Tutin and Clewer), for which, in agreement with these authors and with the constitution assigned to emodin (Oesterle, A., 1912, i, 632), the annexed formula is proposed. The ether was reduced by zinc and acetic acid to emodinanthranol monomethyl ether (physcihydron) (Oesterle and Johann, *loc. cit.*; Hesse, A., 1912, i, 284). No crystalline acetyl derivative could be obtained, but a *dibenzoate*, $C_{30}H_{20}O_6$, was isolated



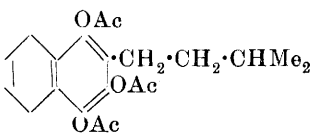
in white needles, which changed to a viscous liquid at about 185°. This was reduced to a non-crystallisable substance, and oxidised by chromic acid to dibenzoylemodin monomethyl ether (dibenzoylphyscion) (*ibid.*). The ether could not be converted into a trimethoxy-compound, which is probably due to the influence of –C·O·C– grouping on the neighbouring hydroxyl groups, neither could it be demethylated without reduction taking place at the same time.

The amounts of the chief constituents of the oxidised chrysarobin were found to be: emodin 0·2%, emodin monomethyl ether 9·3%, chrysophanic acid 22·7%, dehydroemodinanthranol monomethyl ether 18%, amorphous, violet, and brown products 26%. J. C. W.

Derivatives of Lapachol. Lydia Monti (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 1058—1064*).—In accordance with the structural formula ascribed by Paternò (A., 1883, 210) to lapachol, this acid, in alcoholic solution and in presence of palladium black, combines with two atoms of hydrogen, yielding the corresponding colourless quinol, which is immediately reoxidised to lapachol by atmospheric oxygen; the fact that the double linking of the amylene residue is not hydrogenated under the above conditions is probably owing to the negative influence exerted by the phenolic hydroxyl. When the latter is converted into the acetoxy-group, four atoms of hydrogen are absorbed, two being used in reducing the amylenic group and two in converting the quinone into quinol, which is oxidised in the air to the *acetyl* derivative of *dihydrolapachol*, $C_{17}H_{18}O_4$, this forming canary-yellow crystals, m. p. 74—75°. *Dihydrolapachol* (annexed formula) forms yellow needles, m. p. 87—89°.



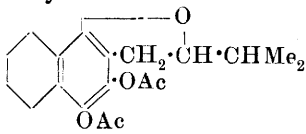
When lapachol acid is heated with acetic anhydride and zinc dust, the double linking of the side-chain remains unchanged, the product being the triacetyl derivative of hydrolapachol obtained by Paternò and Minunni (A., 1890, 1310). In alcoholic solution and in presence of palladium black this compound combines with two atoms of hydrogen, giving *triacetyltetrahydrolapachol* (annexed formula), which forms white needles, m. p. 110—112°, and, when hydrolysed with potassium hydroxide, yields dihydrolapachol, m. p. 87—89° (*vide supra*). Tetrahydrolapachol acid could not be isolated, as it undergoes immediate oxidation.



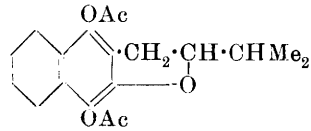
The formation of α- or β-lapachone by the action of an acid on lapachol is not determined by the nature of the mineral acid employed (compare Hooker, T., 1892, **61**, 611), but depends solely on the temperature, α-lapachone being obtained in the hot and the β-isomeride in the cold. A mixture of the two is usually obtained, one or the other predominating according to the temperature. In

* and *Gazzetta*, 1915, **45**, ii, 51—58.

alcoholic solution containing palladium black, both lapachones absorb two atoms of hydrogen, but the colourless reduction products thus formed oxidise immediately in contact with the air. This behaviour is in accord with the formulæ attributed to the lapachones by Hooker, who regarded them as derivatives of α- and β-naphthaquinone respectively.

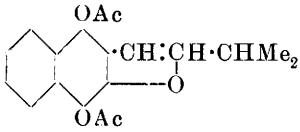


(I.)



(II.)

When β-lapachone, m. p. 156°, is heated with acetic anhydride and zinc dust, it yields diacetylhydro-β-lapachone (I), m. p. 160—162° (compare Paternò and Minunni, A., 1890, 1310); under similar conditions, α-lapachone, m. p. 116—117°, gives *diacetylhydro-α-lapachone* (II), which forms white needles, m. p. 170—172°. Since compound (II) is also obtained by hydrogenation, in presence of palladium black, of Paternò's diacetyl-lapachol (*loc. cit.*), the structure of the latter is probably that annexed, this being one of the formulæ suggested by Hooker (*loc. cit.*).



T. H. P.

Gondang Wax (Cera Fici). A. J. Ultée (*Pharm. Weekblad*, 1915, **52**, 1097—1101).—Gondang wax contains an alcohol, named ficoceryl alcohol by Greshoff and Sack (A., 1901, i, 445). This alcohol has been proved to be identical with β-amyrin, m. p. 196—197°, $[\alpha]_D + 87{\cdot}35°$. Lupeol acetate is also present in Gondang wax.

A. J. W.

Geranyl Chloride. Justin Dupont and Louis Labaune (*Chem. Zentr.*, 1914, II, 932—933; from *Sci. Ind. Rep. Roure Bertrand Fils.*, 1914, [iii], **9**, 3—4. Compare A., 1912, i, 880).—In reference to the paper of Forster and Cardwell (T., 1913, **103**, 1338) the authors state that they have never designated the product of the action of hydrogen chloride on linalool as linalyl chloride, but as geranyl chloride. The thionyl chloride-pyridine method gives with linalool good results, but with geraniol, sulphur-containing substances are also formed, and consequently for the preparation of geranyl chloride the action of hydrogen chloride on geraniol in toluene solution (*loc. cit.*) is preferable. The authors confirm the statement that linalool is the main product of the action of alkalis on geranyl chloride. So, for example, linalool is formed by shaking geranyl chloride with potassium carbonate solution at 100°, and linalyl acetate by the action of potassium acetate.

G. F. M.

Nitrocamphor and its Derivatives. VIII. Action of Formamide on Nitrocamphor. T. M. Lowry and V. Steele (T., 1915, **107**, 1038—1043).—The method already described for the preparation of nitrocamphor (T., 1898, **73**, 995) may advantageously

be modified by using alcoholic sodium ethoxide to reduce the crude bromonitrocamphor. From the cold reaction mixture the sodium salt crystallises out, and on acidification a precipitate of almost pure solid nitrocamphor is obtained in 50% yield from the camphor taken. A theoretical yield may be obtained by oxidising *iso*nitrosocamphor with permanganate. The *ammonium salt* of *nitrocamphor* was obtained as a white, crystalline precipitate by adding formamide to a solution of nitrocamphor in ethyl acetate, or by adding concentrated ammonia to a concentrated solution in acetone. It melts at 178°, and has $[\alpha]_{5461} + 384°$, and $[\alpha]_{5780} + 324°$ in aqueous solution. It is much more stable than is nitrocamphor itself. A new *anhydride* of *nitrocamphor*, $C_{20}H_{28}O_5N_2$, was obtained by boiling a solution of nitrocamphor in ethyl acetate with formamide for twelve hours. On concentration, yellow needles, m. p. 184°, separated, which, although in appearance similar, are not identical with a previously described anhydride, m. p. 193° (T., 1898, **73**, 996). It has $[\alpha]_{5461} - 6°$, and $[\alpha]_{5780} - 4°$, in benzene solution, and it is suggested that the new anhydride is a stereoisomeride of the old.

G. F. M.

Auto-oxidations in Light in the Terpene Series. II. E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 1065—1067). —When pulegone is exposed for six months to the action of light in presence of water and oxygen, it is partly oxidised, as with permanganate, into acetone and β-methyladipic acid, and yields also a *keto-lactone*, $C_{10}H_{14}O_3$, m. p. 183·5°, which forms an insoluble, unstable *silver* salt and an *oxime*, $C_{10}H_{15}O_3N$, m. p. 116°, and gives acetone and β-methylglutaric acid on oxidation with chromic acid. The results obtained on exposing other cyclic ketones to the action of light, in either absence or presence of oxygen, indicate that the structure of the keto-lactone is $CMe_2{:}C\begin{<}O{-}CO{-}CH_2 \\ CO{\cdot}CH_2{\cdot}CHMe\end{>}$, and that it is formed from pulegone by way of the intermediate compound,

$$CMe_2{:}C(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H.$$

T. H. P.

Ethereal Oils. SCHIMMEL & Co. (*Chem. Zentr.*, 1915, i, 1264—1265; from Schimmel's *Geschäftsber.*, Oct., 1914–April, 1915).—Ammoniacum oil is a yellow oil of peculiar odour, D^{15} 0·8875, n_D^{20} 1·47250, acid number 3·7, ester number 40·5, acetyl ester number 106·4; it is soluble in 0·5 and more vols. of 90% alcohol.

Pine needle oils.—Oil from *Pinus heterophylla*, D^{15} 0·8879, n_D^{20} 1·48568, α_D −35°23′, acid number 0·6, ester number 10·1; it is soluble in 7 vols. and more of 90% alcohol to a cloudy solution. *l*-α-Pinene, *l*-β-pinene, and probably camphene are present. Oil from *Pinus palustris* has D^{15} 0·8844, n_D^{20} 1·48277, α_D 30°15′, acid number 0·9, ester number 4·6. It dissolves with faint opalescence in 6 vols. of 90% alcohol and contains *l*-α-pinene and *l*-β-pinene. Oil from *Pinus ponderosa* has D^{15} 0·8796, n_D^{20} 1·48033, α_D −17°16′, acid number 0·6, ester number 8·6. It is soluble in 5·5 parts and more of 90% alcohol. It contains *l*-α-pinene and *l*-β-pinene.

The oil described in the reports of October, 1905, and April, 1908 (compare A., 1908, i, 666), is derived from *Lavandula dentata*, L., not from *Lavandula stoechas*.

Mastix oil contains small quantities of inactive α-pinene and of an unidentified terpene in addition to much *d*-α-pinene. The solid acid of musk kernel oil is palmitic acid. A pale brown oil is obtained in 0·5% yield from *Amomum Melegueta*, Roscoe, which has D_D^{15} 0·8970, n_D^{20} 1·49116, α_D −3°10′, acid number 2·7, ester number 41·2, acetyl ester number 63·9. It is miscible with an equal volume of 95% alcohol, but when more alcohol is added a turbidity ensues. Roman camomile oil is occasionally lævorotatory (−2°30′). Syrian sage oil contains camphor and, probably, also thujone.

Copalillo oil, extracted from a Mexican wood, probably *Exothea Copalillo*, is a brownish-yellow substance, D^{15} 0·8504, α_D +0°50′, acid number 10·2, ester number 13·1, soluble in 0·5 and more vols. of 90% alcohol. The *oil* from a Bombay wood, probably a variety of *Artemisia maritima*, is dark green, D^{15} 0·9696, acid number 1·8, ester number 4·2. It dissolves in about 3 vols. of 70% alcohol with separation of paraffin.

Oils from Hernandia peltata. In four experiments wood from the stem gave 1·03—2·06% yields. The *oil* has D^{15} 0·958—0·963, α_D +83°45′ to +104°12′, n_D^{20} 1·49695—1·50111, acid number 4·4, ester number 47·1, aldehyde content (with neutral sulphite) 75—80%. It is soluble in 2·5—4 vols. of 70% alcohol with occasional slight fluorescence. The *oil* from the root was obtained in 0·5% yield, and had D^{15} 0·9667, n_D^{20} 1·50383, α_D +126°15′, aldehyde content 92·5%. It dissolves in 2·5 and more vols. of 70% alcohol. *Oil* from the entire fruit: yield 0·5%, D^{15} 0·9528, n_D^{20} 1·49554, α_D +50°16′, aldehyde content 49%. It dissolves in 0·3 and more vols. of 90% alcohol, but does not give a clear solution with 10 vols. of the 80% solvent. *Oil* from the almond-like kernel: yield 1·38%, D^{15} 1·0044, n_D^{20} 1·50614, α_D +87°, acid number 7·3, ester number 110·4. It is not completely soluble in 10 vols. of 70% alcohol, but gives an opalescent solution with 0·5 vol. 80% alcohol. All the oils are pale to deep yellow in colour, and, with exception of the fruit oil, have a characteristic odour of Perilla aldehyde.

Himalaya Cedar Oil is obtained as a pale brown substance, with the odour of balsam, from *Cedrus Deodora* and *C. Libani Barrel var. Deodora*. It has D^{15} 0·9530, n_D^{20} 1·51565, α_D +53°8′, acid number 2·9, ester number 14·9, acetyl ester number 39·2. It is not quite completely soluble in 10 vols. of 90% alcohol, miscible with 95% alcohol. It appears to contain the ketone (semicarbazone, m. p. 158°) identified in Atlas Cedar oil. The sesquiterpene could not be identified; tests for cadinene did not give a positive result.

The *oil* from *Libocedrus decurrens* (California) has D^{15} 0·8756, n_D^{20} 1·47544, α_D −0°51′, acid number 0·9, ester number 4·6. It dissolves in 7 or more vols. of 90% alcohol to a turbid solution. It contains *l*-α-pinene, and, probably, β-pinene and carvone.

The *oil* from the leaves of *Melaleuca hypericifolia* has a pale green colour with the odour and properties of the oil of *Eucalyptus globulus*. It has D^{15} 0·9145, n_D^{20} 1·46271, α_D +0°18′, and is soluble in

2·5 and more vols. of 70% alcohol. It contains 72% of eucalyptol. *Oils* from *Melaleuca leucadendron var.* Two plants of the Cajeput class, raised in Amani, gave oils differing from that of Cajeput. The narrow-leaved variety contains only a small quantity of eucalyptol, which is completely absent from the broad-leaved variety. The oil from the latter contains 78% methyleugenol (veratric acid, m. p. 179·5°), but methylchavicol could not be identified. It has D^{15} 1·0019, n_D^{20} 1·52500, α_D − 3°44′, acid number 0·4, ester number 7·6, acetyl ester number 15·2; it dissolves in 0·6 and more vols. of 90% alcohol. The oil from the narrow-leaved variety has D^{15} 0·9056, n_D^{20} 1·47936, α_D − 0°22′, acid number 0·7, ester number 11·8, acetyl ester number 84·8. It is soluble in 1·5 and more vols. of 80% alcohol.

Clove tree oil has D^{15} 1·0933, n_D^{20} 1·54332, α_D − 3°11′, phenol content 88%. It dissolves in 1·8 and more vols. of 70% alcohol. The phenols consist of 60% eugenol (53% of the total oil) and 35% of a solid *phenol* of paraffin-like odour. The latter has m. p. 44—45·5°, b. p. 309—310°/754 mm., 146—149°/4 mm., D^{15} 1·188. It is inactive, and yields a *benzoyl* derivative, m. p. 87—88°.

A pale yellow oil, with a strong odour of camphor, is obtained in 1·7—2·1% yield from Japanese wild cinnamon bark. It has D^{15} 0·9245, n_D^{20} 1·4779, α_D + 8°34′, acid number 0·6, ester number 14·8. It is soluble in 1 or more vols. of 80% alcohol. The main constituent is camphor, but terpenes and cymol appear to be also present.

H. W.

American Colophony. Ludwig Paul (*Chem. Zentr.*, 1915, i, 1265—1266; from *Seifensieder Zeit.*, 1915, **42**, 237—238, 258—259, 285—286, 307).—The author's conclusion (compare A., 1914, i, 976) that substances of low m. p. form the chief constituents of colophony is contradictory to the statements of Tschirch and others who have been able to isolate substances, m. p. 135°. The difference is explicable, since alcohol was used in the separation of the individual components, and this removes the colloidally combined water. Actually, sylvic acid (KA resin acid), m. p. 120—123°, could be isolated by the action of 90% alcohol on colophony or KS resin acid. The results of previous investigations are summarised as follows: Colophony is a product containing colloidally combined water from which two amorphous substances with differing water content can be separated: γ-pinic acid (KS acid), first m. p. 70—71°, second m. p. 76—77° (90% of colophony), sylvic acid (KA) from KS acid with boiling alcohol (90%), m. p. 122—123°. In course of time, each of these yields α-pinic acid, m. p. 100—105°, and β-pinic acid, m. p. 122—123°, both of which are soluble in water containing lime. The α-, β-, and γ-abietic acids, m. p. about 150°, 160° and 162° respectively, obtained from the above compounds by protracted crystallisation from hot alcohol, are stable. KLw (α-pinic acid) is obtained in the concentrated alkaline mother liquors from β- and γ-pinic acids, and is probably present to a small extent in colophony.

Finally, the author draws attention to the fact that there can only be one abietic acid, namely, the γ-form. γ-Pinic acid is not a true

acid; on the other hand, α- and β-pinic acids derived from it are well characterised acids giving clear solutions with alkalis. H. W.

Colophony Resin. Ludwig Paul (*Chem. Zentr.*, 1915, i, 1266; from *Chem. Rev. Fett-Harz-Ind.*, 1915, **22**, 30—33. Compare preceding abstract).—A resinous product is obtained by the author from the syrupy, alcoholic mother liquors of colophony or from the ethereal solution of KS-acid after the latter has been freed from resin acid by treatment with ammonia and ammonium carbonate. The yield obtained by the latter process is so great that it suggests the formation of resin by the action of alkali. A substance, which can be compared with the resin of Tschirch, is prepared by the author by dissolving colophony dust in alcohol, treatment with ammonia and water, filtration, extraction of the residue with sodium hydroxide, and solution in alcohol; the product is poured into sodium hydroxide solution, then acidified with hydrochloric acid, and again precipitated by alkali hydroxide. It is a white powder, m. p. ca 98°, insoluble in alkali, readily soluble in alcohol and ether. In these experiments, α- and β-pinic acid were identified for the first time in the presence of one another.

The formation of colophony powder takes place in two stages, characterised by α- and β-pinic acids. H. W.

The Glucosidification of Glycerol by α-Glucosidase. Em. Bourquelot, M. Bridel, and A. Aubry (*Compt. rend.*, 1915, **161**, 41—43).—The authors have examined the action of α-glucosidase in bottom yeast on an aqueous mixture of dextrose and glycerol under the same conditions as in the case of β-glucosidase (compare this vol., i, 703). The results show that glucosidification took place, but no crystalline product could be isolated. Measurements of rotation and determination of the amounts of dextrose formed on hydrolysis indicated that the products of the action were two monoglucosides having rotatory powers of slightly above +129° and inferior to +120° respectively. W. G.

Fluorescence of the Components of Chlorophyll. A. Wilschke (*Chem. Zentr.*, 1915, i, 1173—1174; from *Zeitsch. wiss. Mikroscop.*, 1915, **31**, 338—361).—The author has confirmed the observations of Cvet and Willstätter that the chlorophyll of green plants is composed of two fluorescent substances, (*a*) having a band at λ 68—65·5, and (*b*) with the band at λ 65·8—65·3. The chlorophyll of *Phaeophyceae*, *Diatomaceae*, and *Hydrurus* is quite different; in the living state it exhibits only one band, identical with that of (*a*), whilst when dead or in alcoholic solution it gives a second band at λ 64·0—63·0, which is quite distinct from that of (*b*), and corresponds with the chlorophyll component (*c*), detected in *Phaeophyceae* by Cvet, but the existence of which is denied by Willstätter. The chlorophyll of *Neottia nidus avis* contains only the component (*a*). The inactivity of the chlorophyll is possibly connected with the absence of the other components. H. W.

Bile Pigments. VIII. Bilirubin. William Küster [with H. Bauer, K. Reihling, and A. Schwaderer] (*Zeitsch. physiol. Chem.*, 1915, **94**, 136—162).—A number of reactions of bilirubin

are described, chiefly in extension of earlier work (A., 1913, i, 210; 1914, i, 857), and a probable formula for bilirubin, which agrees with most of the facts, is given.

When freshly crystallised bilirubin is recrystallised from dimethylaniline, only about 67% separates from the solution, and it is found that the remaining third has undergone change and contains a substance with m. p. 134—136°. This is explained by assuming that bilirubin is a mixture of two modifications, the equilibrium of which is disturbed by the solvent. It is not due to decomposition, for the balance is not altered any more by prolonged boiling of the solution.

By the action of methyl sulphate on bilirubin in the presence of methyl-alcoholic sodium hydroxide, a dark green, non-crystallisable dimethyl ester is obtained, but in aqueous alkaline solution the methylation is not so complete. When esterified by means of methyl alcohol and hydrochloric acid (*loc. cit.*) even in an atmosphere of hydrogen, the product is green. This development of colour also occurs when bilirubin is warmed with glacial acetic acid or mono- or trichloro-acetic acids, but not with their esters or with formic acid (compare Maly, 1875), and is explained by assuming that there is in bilirubin an internal salt which is opened by acids of a certain strength, the new modification being less stable and, especially, much more sensitive towards oxygen than the original. If the acid is stronger, however, it may form a salt with bilirubin itself. Thus hydrogen chloride gradually precipitates from a solution of bilirubin in chloroform, a product of approximately the formula

$$(C_{32}H_{36}O_6N_4)_2,3HCl,$$

which has a cantharides-like colour, whilst the solution contains another chlorine derivative.

Further attempts to prepare a crystalline dimethylbilirubin led to a study of the action of hydrogen bromide in glacial acetic acid, followed by methyl alcohol, and also of the effect of diazomethane on bilirubin, but with indefinite results. The latter agent seems to combine directly with the pigment besides forming a dimethyl compound.

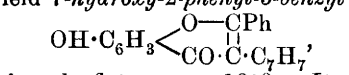
When a suspension of bilirubin in dry methyl alcohol is treated with dry ammonia, a solution results which deposits *bilirubin-ammonia*, $C_{32}H_{36}O_6N_4,NH_3$, when left in a freezing mixture. This substance forms stable brownish-red crystals, dissolves in sodium hydrogen carbonate, and is reconverted into bilirubin on boiling with chloroform. Using this regenerated bilirubin, the yield of the ammonia compound is about 76%. Older preparations give 50—60% yields, whilst very old specimens give practically no deposit. This, again, is supposed to indicate that bilirubin contains two modifications in equilibrium, one of which is favoured by ammonia. The alcoholic mother liquor apparently contains the other modification as a soluble ammonium salt, because a compound of this nature is precipitated in yellowish-red flocks on diluting with much ether. On boiling the solution with an excess of dilute sulphuric acid, however, a voluminous precipitate is obtained. This contains a part insoluble in chloroform, an almost black oxidation *product*, $C_{32}H_{33}O_9N_5$, similar to but not identical with bilinigrin (*loc. cit.*), a part moderately soluble in chloroform and soluble in sodium carbonate, consisting of ordinary bilirubin, and an

extremely soluble part, soluble in sodium hydrogen carbonate, which is the *aci*-form of bilirubin. Bilirubin-ammonia gives a pale brown trimethylated compound with diazomethane.

When treated with stannic or aluminium chlorides in inert solvents, bilirubin gives dark red precipitates. In this respect it corresponds with aromatic ketones and quinones (Meyer, A., 1908, i, 731; 1910, i, 179), but the colours do not revert to the original, but change to green on the addition of water, showing that the pigment has undergone change. J. C. W.

Bile Pigments. IX. Formation of Gall Stones. William Küster [with K. Reihling] (*Zeitsch. physiol. Chem.*, 1915, **94**, 163—171).—After removing various constituents of gall stones by means of ether, hot water, 10% acetic acid and then ether, complete exhaustion with cold alcohol dissolves a mixture of derivatives of the basal group of the pigment part of hæmoglobin with fatty acids or wax-like esters. Oxidation of the mixture gave hæmatic acid. After now removing the bulk of the bilirubin by means of chloroform, glacial acetic acid extracts choleprasin, leaving "bilihumin" (A., 1914, i, 858). Choleprasin has now been hydrolysed by means of fuming hydrochloric acid. The black, insoluble part corresponds with bilinigrin, the oxidation product of bilirubin, since it gives an insoluble sodium salt. On oxidation with nitric acid, it yields an alcohol, m. p. 51·5°, not identical with cholesterol or coprosterol, and also hæmatic acid. The hydrochloric acid solution contains most of the "Bausteine" of globin, including histidine, which was isolated, but no tyrosine or tryptophan could be detected. Choleprasin also contains wax-like esters, which are supposed to be compounded of alcohols and acids, the origin of which is due to the operation of processes of reduction (such as are caused by ferments and putrefactive moulds) on the amino-acids of globin. In the change of hæmoglobin to choleprasin, therefore, the pigment part is oxidised and the globin part reduced. J. C. W.

Syntheses of γ-Benzopyrones and Flavones. II. Serge Jacobson and Brojendranath Ghosh (T., 1915, **107**, 959—966).—The condensation of substituted acetoacetic esters with phenols with the production of substituted γ-benzopyrones (this vol., i, 424) takes place also with substituted benzoylacetoacetic ester, substituted flavones being formed. Thus benzylbenzoylacetic ester and resorcinol in presence of dry hydrogen chloride yield *7-hydroxy-2-phenyl-3-benzyl-γ-benzopyrone*,



which forms colourless leaflets, m. p. 186°. It dissolves in sodium hydroxide to a yellow solution, and in sulphuric acid with the production of an intense bluish-violet fluorescence. Its *acetyl* derivative melts at 134°. Its constitution is confirmed by its decomposition by boiling alkali hydroxide into benzylacetophenone and β-resorcylic acid. Similar condensation products are formed with other phenols in presence of hydrogen chloride, zinc chloride, etc. Thus pyrogallol condenses with ethyl β-benzoyl-α-phenylpropionate to form 7 : 8-*dihydroxy*-2-

phenyl-3-benzyl-γ-benzopyrone, colourless leaflets, m. p. 136—137°, which dissolve in sodium hydroxide to give a reddish-brown sodium salt, and in sulphuric acid to a yellow solution which develops a green fluorescence. α-Naphthol condenses to give *2-phenyl-3-benzyl-1 : 4-α-naphthapyrone*, m. p. 71·5°, phloroglucinol yields 90% of the theory of *5 : 7-dihydroxy-2-phenyl-3-benzyl-γ-benzopyrone*, brown prisms, m. p. 119°, giving an *acetyl* derivative, m. p. 56°, and orcinol a small quantity of *7-hydroxy-2-phenyl-3-benzyl-5-methylbenzo-γ-pyrone*, lemon-yellow needles, m. p. 108°. αγ-Diphenylacetoacetic ester could not be made to condense with resorcinol or pyrogallol; instead, 1 : 3-dihydroxy-2-phenylnaphthalene was formed by elimination of alcohol from the ester. G. F. M.

Syntheses of γ-Benzopyrones and Flavones. III. SERGE JACOBSON and BROJENDRANATH GHOSH (T., 1915, **107**, 1051—1058).—Ethyl α-phenylacetoacetate condenses with resorcinol, pyrogallol, and α-naphthol in presence of sulphuric acid, and with phloroglucinol in presence of zinc chloride, to give the following substituted γ-benzopyrones respectively: *7-Hydroxy-3-phenyl-2-methyl-γ-benzopyrone*,

$$OH\cdot C_6H_3\!<\!\begin{matrix}O\text{—}C\cdot Me\\ \|\\ CO\cdot C\cdot Ph\end{matrix},$$

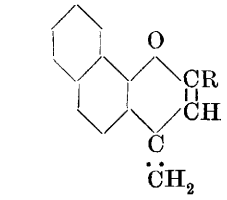
colourless needles, m. p. 226°, which dissolve in sodium hydroxide and in sulphuric acid to give fluorescing solutions. It gives colourless *acetyl* and *benzoyl* derivatives melting at 185° and 187—188° respectively, and *ethyl* and *methyl* ethers melting at 89—90° and 87° respectively. On decomposition with potassium hydroxide, it gives β-resorcylic acid and benzyl methyl ketone. *7 : 8-Dihydroxy-3-phenyl-2-methyl-γ-benzopyrone*, pale yellow prisms, m. p. 268°. The *acetyl* derivative melts at 211°, the *benzoyl* derivative at 204°, and the *ethyl ether* at 132°. *3-Phenyl-2-methyl-1 : 4-α-naphthapyrone*, lemon-yellow needles, m. p. 209°, which develop a dark green fluorescence in sulphuric acid. *5 : 7-Dihydroxy-3-phenyl-2-methyl-γ-benzopyrone*, lemon-yellow needles, m. p. 178°. The *acetyl* derivative melts at 146°.

Resorcinol and ethyl α-phenylformylacetate condense when heated with zinc chloride to give a poor yield of *7-hydroxy-3-phenyl-γ-benzopyrone*,

$$OH\cdot C_6H_3\!<\!\begin{matrix}O\text{—}CH\\ \|\\ CO\cdot CPh\end{matrix},$$

yellow needles, m. p. 131°, which dissolve in sodium hydroxide to a red solution and give a green fluorescence in alcoholic or sulphuric acid solution. Ethyl acetylmalonate and ethyl benzoylacetate do not yield γ-benzopyrones with resorcinol, the only products separated being β-methyl- and β-phenyl-umbelliferon respectively. G. F. M.

Synthesis of α-Naphthapyranols. BROJENDRANATH GHOSH (T., 1915, **107**, 739—744).—The similarity in the behaviour of α-naphthol and *m*-dihydroxy-phenols with respect to the formation of pyrone derivatives (Ghosh and Jacobson, T., 1915, **107**, 424) is also maintained in their behaviour towards acetylacetone and benzoylacetone,



α-naphthol readily undergoing condensation with these diketones yielding α-naphthapyranols of the annexed constitution.

Collie and White's suggestion (T., 1915, **107**, 369) that the colour of the compounds, obtained from *m*-dihydroxyphenols and these ketones, may be due to a quinonoid structure is supported by the fact that the α-naphthapyranols, to which a quinonoid arrangement cannot be assigned, are almost colourless.

2-*Methyl*-4-*methylene*-1 : 4-α-*naphthapyranol*, prepared by heating α-naphthol and acetylacetone with phosphoryl chloride at 100—105°, forms pale buff-coloured needles, which slowly turn green on exposure to air, decomp. 166° with previous colour change at 150°. Its constitution has been established by the formation of 1-hydroxy-β-naphthyl methyl ketone on fusion with potassium hydroxide. The following salts are described: *picrate*, yellowish-green needles, m. p. 159° (decomp.), yellowish-brown *mercurichloride*, explosive *perchlorate*, *platinichloride*, *aurichloride*, and yellow, crystalline *hydrochloride*, m. p. 96° (decomp.).

2-*Phenyl*-4-*methylene*-1 : 4-α-*naphthapyranol*, prepared in a similar manner from benzoylacetone, changes colour at 115°, m. p. 125° (decomp.), and yields a *picrate*, yellowish-green needles, m. p. 165°, amorphous, brown *mercurichloride*, *perchlorate*, long, green needles, and *platinichloride*, brown needles. F. B.

Precipitation of Quinine Salts in Salt Solutions. Francesco Lenci (*Chem. Zentr.*, 1915, i, 1269; from *Giorn. Farm. Chim.*, 1915, **64**, 154—160).—The results obtained by Tarugi (A., 1914, i, 571) are confirmed. H. W.

Ephedrine and ψ-Ephedrine. Ernst Schmidt (*Arch. Pharm.*, 1915, **253**, 52—61).—I. *β-Methylaminopropylbenzene*: The assumption that the transformation of ephedrine into ψ-ephedrine, and vice versa, is due to the rearrangement of the -CH·OH group in space (A., 1914, i, 989) is supported by the fact that the nearly related β-methylaminopropylbenzene ($NHMe\cdot CHMe\cdot CHPh\cdot OH \longrightarrow NHMe\cdot CHMe\cdot CH_2Ph$) is not isomerised by heating with hydrochloric acid, that is, under the conditions favourable to the above changes.

II. *Methylephedrine methyl hydroxide.*—The chief reaction which takes place when an aqueous solution of this compound is distilled is represented by the equation $OH\cdot CHPh\cdot CHMe\cdot NMe_3\cdot OH = NMe_3 + H_2O + \left[C_6H_5\cdot COEt + CHPh\cdot CHMe \atop \quad\quad\quad\

III. *Methylephedrine methiodide.*—It has been shown (Emde, A., 1909, i, 565, 709) that quaternary ammonium salts lose the basic group when treated with sodium amalgam. The present salt also behaves in this way, giving trimethylamine and phenylpropylene oxide, thus: $OH\cdot CHPh\cdot CHMe\cdot NMe_3I + NaOH = H_2O + NaI + NMe_3 + CHPh\cdot CHMe$. This reaction is also complicated by the formation of methylephedrine, ephedrine, and the tertiary base compounded of the latter with phenylpropylene oxide (see following abstract). The latter compound has been prepared directly by heating ephedrine and alcoholic phenylpropylene oxide in a sealed tube. J. C. W.

Ephedrine and Related Compounds. August Eberhard (*Arch. Pharm.*, 1915, **253**, 62—91. Compare preceding abstract).—Methylephedrine methiodide (A., 1906, i, 978) was converted into the *methochloride*, $OH\cdot CHPh\cdot CHMe\cdot NMe_3Cl,H_2O$, large, transparent, rectangular tablets, m. p. 230°, by shaking a solution with silver chloride. A solution of the methyl hydroxide, prepared by the action of moist silver oxide, deposited methylephedrine after a time. A quantity of the solution was distilled almost to dryness and the distillate was extracted with ether. The extract was shaken with very dilute hydrochloric acid and the remaining oil was allowed to crystallise and then pressed on filter paper. The crystals consisted of methylephedrine, which was found to be very volatile. The oil which had been absorbed by the paper was again dissolved and treated with dilute hydrochloric acid. The combined solutions of the hydrochlorides were evaporated, and the salts were separated by fractional crystallisation from water and acetone, and by means of the aurichlorides. Trimethylamine, methylephedrine, ephedrine, and small quantities of ephedrine-phenylpropylene oxide (see below) were isolated.

A hot 20% solution of methylephedrine methiodide was also treated with sodium amalgam. The hot liquid was freed from trimethylamine by a current of air, and then cooled and extracted with ether. The extract was shaken with dilute hydrochloric acid and this solution was crystallised. The first crystals represented the chief product, namely, the double compound of ephedrine hydrochloride with phenylpropylene oxide, whilst the mother liquor contained ephedrine and methylephedrine. The small amount of non-basic products had the odour of dill and estragon.

Ephedrine-phenylpropylene oxide, $C_{10}H_{15}ON,C_9H_{10}O$, crystallises in colourless tablets, m. p. 125°, $[\alpha]_D^{15} - 3{\cdot}59°$, and forms a *hydrochloride*, compact, transparent tablets, m. p. 155—156°, $[\alpha]_D^{15} + 14{\cdot}74°$, an *aurichloride*, slender needles or leaflets, m. p. 144—145°, a *platinichloride*, m. p. 176·5—177°, and a *dibenzoate*, $C_{19}H_{23}N(OBz)_2$, m. p. 141—142°. When left for some days with methyl iodide, it formed a *methiodide*, m. p. 183°, which yielded a *methochloride*, m. p. 203°, but when heated with an excess of the reagent at 100° it gave an isomeric *methiodide*, m. p. 164°, which, in turn, formed a *methochloride*, m. p. 165—167°, and a *platinichloride*, m. p. 185°. Ephedrine-phenylpropylene oxide is, therefore, a tertiary base with two hydroxyl groups.

Attempts to Prepare an Inactive Ephedrine (compare Calliess, A., 1912, i, 365).—The conversion of α-aminopropiophenone into a monomethyl derivative could not be realised. Diazomethane gave no methyl compound, and methyl iodide and methyl sulphate yielded small quantities of the dimethyl derivative, but chiefly the quaternary salt (Calliess). The corresponding carbinol, $OH\cdot CHPh\cdot CHMe\cdot NH_2$, was also shaken with methyl iodide, and the product was dissolved in water and shaken with silver oxide and ether. The extract contained a small amount of the tertiary base, which formed a *methiodide*, $OH\cdot CHPh\cdot CHMe_2I$, m. p. 221°, whilst the mother liquor contained the quaternary base, which was converted into the aurichloride and platinichloride (Calliess). These inactive quaternary compounds are isomeric with the methyl derivatives of ephedrine and ψ-ephedrine. ω-Aminobenzylmethylcarbinol behaved similarly, yielding the tertiary base and quaternary iodide (Schmidt, A., 1911, i, 742; Emde, A., 1910, i, 479). *ω-Dimethylaminobenzylmethylcarbinol hydriodide*, $OH\cdot CHMe\cdot CHPh\cdot NMe_2,HI$, forms colourless prisms, m. p. 220—221°.

As an alternative to these abortive attempts to methylate suitable amino-compounds, the action of methylamine on α-bromopropiophenone has been tried (compare Goehring, A., 1909, i, 322). When alcoholic solutions were left together for several days, the methylation proceeded too far. The aurichloride, m. p. 168·5—169°, and the platinichloride, m. p. 188°, of the product agreed in composition but not in m. p. with the quaternary compounds, $CHMeBz\cdot NMe_3X$. When the reagents were mixed at 0° in benzene solution, however, most of the ketone escaped reaction, but, on shaking the solution with 12·5% hydrochloric acid, evaporating and crystallising the dry salts from alcohol, the *hydrochloride* of *α-methylaminopropiophenone*, $CHMeBz\cdot NHMe,HCl$, was eventually obtained, in colourless crystals, m. p. 179° (*aurichloride*, m. p. 120°, *platinichloride*, m. p. 187°). This was reduced by sodium amalgam and dilute hydrochloric acid in the cold, when a *base*, $OH\cdot CHPh\cdot CHMe\cdot NHMe$, slender needles, m. p. 114—115°, was finally isolated (*hydrochloride*, m. p. 180—181°, *aurichloride*, m. p. 126°, *platinichloride*, m. p. 190—191°). This base is similar to ψ-ephedrine.

J. C. W.

Extraction of Stachydrine. N. T. Deleano (*Chem. Zentr.*, 1914, ii, 647—648; from *Bul. Soc. de Ştiinţe Bucureşti*, 1914, **23**, 39—42).—The phosphotungstic acid method for the isolation of choline, betaine, and particularly of stachydrine can be replaced by extracting the base with an alcoholic solution of mercuric chloride. Stachydrine has $[\alpha]_D^{18} - 26·2°$, but this value sinks to $-9·2°$ to $-9·3°$ if the base remains long in contact with acids or alkalis, and if boiled with concentrated alkalis it is completely racemised. G. F. M.

Yohimbine (Quebrachine). George Barger and Ellen Field (T., 1915, **107**, 1025—1030).—The authors have confirmed the formula of Spiegel, $C_{22}H_{28}O_3N_2$, for *yohimbine*, and also the presence of one methoxy-group. The *methiodide*, m. p. 250°, even when prepared from the anhydrous base, contains an additional molecule of water analogous to the corresponding compounds of cotarnine and hydrastinine.

Monobromoyohimbine hydrobromide was obtained as microcrystalline aggregates, m. p. 296—298°, by treating the alkaloid with one molecular proportion of bromine, and on further treatment with bromine in chloroform solution the *hydrobromide of dibromoyohimbine* separates. It crystallises in small needles, m. p. 296°. The presence of a benzene nucleus in yohimbine is further indicated by the formation *yohimbinesulphonic acid*, $C_{22}H_{28}O_6N_2S$, m. p. 292—295°, by the action of cold concentrated sulphuric acid. The oxidation of yohimbine with permanganate, nitric acid, and hydrogen peroxide was tried, but without very definite results. On the other hand, from the products obtained by the degradation of the yohimbic acid, prepared by boiling the alkaloid with alkali, by dry distillation with soda-lime, was isolated a *picrate*, $C_{10}H_{12}N,C_6H_3O_7N_3$, m. p. 154—155°, which may be that of a dimethyl- or an ethyl-indole, and also a second *picrate*,

$$C_{11}H_{11}N,C_6H_3O_7N_3,$$

which, although not identified, is thought to contain a pyridine ring associated with a benzene ring, and to contain the basic nitrogen atom of yohimbine. G. F. M.

Production of Picrates of Alkylpyridinium and Analogous Bases. R. (FRH.) VON WALTHER (*J. pr. Chem.*, 1915, **91**, 329—331).—When heated with 2 : 4 : 6-trinitrophenetole, pyridine and similar cyclic bases are converted into the picrates of the corresponding *N*-ethyl quaternary bases.

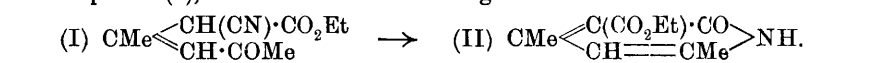
N-Ethylpyridinium picrate, $C_{13}H_{12}O_7N_4$, crystallises in yellow leaflets, m. p. 91°, dissolves in water with slight decomposition, is stable towards alcoholic ammonia, and is converted by hydrochloric acid into picric acid and *N*-ethylpyridinium chloride, which was isolated in the form of its *platinichloride*, m. p. 197°. It may also be prepared by heating pyridine picrate or a mixture of picric acid and pyridine with ethyl orthoformate at 130—140°. Attempts to prepare a similar compound from 2 : 4-dinitrophenetole were unsuccessful.

N-Ethylquinolinium picrate, prepared from 2 : 4 : 6-trinitrophenetole and quinoline, forms yellow leaflets, m. p. 151°. F. B.

Production of Picrates of Alkylpyridinium and Analogous Bases. MORITZ KOHN (*J. pr. Chem.*, 1915, [ii], **91**, 468).—In connexion with Walther's paper (preceding abstract) the author points out that he has already shown (A., 1914, i, 83) that 2 : 4 : 6-trinitroanisole reacts with a number of tertiary bases of widely differing structure to form the picrates of the corresponding *N*-methylated quaternary bases. F. B.

Condensation of Ethyl Cyanoacetate and Acetylacetone. JOHN LIONEL SIMONSEN and MUDLAGIRI NAYAK (T., 1915, **107**, 792—798).—With the object of synthesising an allene derivative of the constitution $CO_2Et\cdot CH(CN)\cdot CMe{:}C{:}CMe\cdot CH(CN)\cdot CO_2Et$, capable of exhibiting enantiomorphous isomerism, the authors have investigated the condensation of acetylacetone and ethyl cyanoacetate by means of diethylamine, but find that the main product of the reaction consists of ethyl 4 : 6-dimethyl-2-pyridone-3-carboxylate (II), formed by the

condensation of one molecule of ethyl cyanoacetate and one of acetylacetone, and subsequent intramolecular rearrangement of the resulting compound (I), as shown in the following scheme :

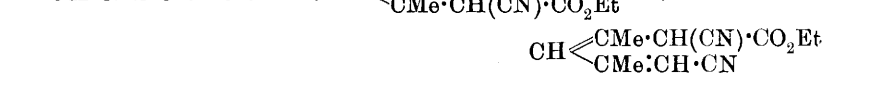


The identity of the ester was established by its hydrolysis with aqueous potassium hydroxide to 4 : 6-dimethyl-2-pyridone-3-carboxylic acid, slender irridescent needles containing $1H_2O$, decomp. 247° (Knoevenagel and Cremer, A., 1902, i, 640, give 254°, presumably for the anhydrous substance) and also by its conversion by means of hydrochloric acid into ψ-lutidocarbostyril, which forms a *picrate*, glistening, yellow prisms, m. p. 155—156°, and a hydrochloride, crystallising with $1H_2O$ and not $2H_2O$ as stated by Hantzsch (A., 1885, 397).

Ethyl 5-bromo-4 : 6-dimethyl-2-pyridone-3-carboxylate, obtained by brominating the ester in chloroform solution, forms silky needles, m. p. 199°, and is hydrolysed by aqueous alkalis to the corresponding *acid*, glistening leaflets, decomp. 255—256°.

1 : 4 : 6-*Trimethyl-2-pyridone-3-carboxylic acid*, prepared from ethyl 4 : 6-dimethyl-2-pyridone-3-carboxylate by methylation with methyl iodide and methyl alcoholic sodium methoxide and subsequent hydrolysis with potassium hydroxide, forms slender, irridescent needles, m. p. 210°, and yields sparingly soluble *lead* (colourless prisms) and *copper* (pale blue needles) salts. Its constitution has been proved by its conversion at 270° into 1 : 4 : 6-trimethyl-2-pyridone, which was isolated in the form of its 3 : 5-dibromo-derivative, m. p. 169—170° (Hantzsch, *loc. cit.*, gives 173°).

In addition to ethyl 4 : 6-dimethyl-2-pyridone-3-carboxylate, the condensation of acetylacetone and ethyl cyanoacetate yields a small amount of a substance, slender needles, m. p. 190—191°, which the authors suggest is *ethyl* $\alpha\epsilon$-*dicyano-*$\beta\delta$-*dimethyl-*$\Delta^{\beta\delta}$-*hexadienoate*, formed by the interaction of two molecules of the cyanoacetate and one of acetylacetone, with elimination of a carbethoxy-group, thus :



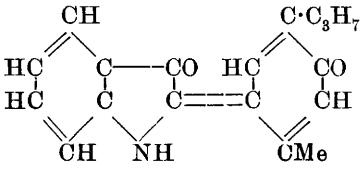
This substance yields a bromo-derivative, possibly *ethyl* α-*bromo-*$\alpha\epsilon$-*dicyano-*$\beta\delta$-*dimethyl-*$\Delta^{\beta\delta}$-*hexadienoate*, yellow needles, m. p. 196°.

F. B.

Quinoline Compounds and Process for Producing the Same. A. B. Davis (U.S. Pat. 1138936, 1138937 ; from *J. Soc. Chem. Ind.*, 1915, **34**, 685).—I. By boiling a solution, in absolute alcohol, of pyruvic acid, vanillin, and an aromatic amine, a derivative of quinoline-4-carboxylic acid is formed having a *p*-hydroxy-*m*-methoxyphenyl group in the 2-position in the quinoline ring and the hydrogen of one of the CH-groups replaced by an organic radicle, the position and nature of which are determined by the aromatic amine used, *p*-toluidine, for example, giving the 6-methylquinoline derivative.

II. The condensation of an ester of *p*-aminobenzoic acid, an aromatic aldehyde, and pyruvic acid by boiling the substances together in absolute alcoholic solution results in the formation of an ester of quinoline-4 : 6-dicarboxylic acid having an aryl group in the 2-position of the quinoline ring. G. F. M.

A New Derivative of Indoxyl. ADOLF JOLLES (*Monatsh.*, 1915, **36**, 457—470).—In a previous communication (A., 1913, ii, 892), the author has suggested a method of detecting indican in which urine, after treatment with lead acetate solution, is oxidised by ferric chloride and hydrochloric acid in the presence of thymol; when the resultant solution is shaken with chloroform, a violet coloration is developed, whereby the presence of minute quantities of indican can be detected. The present paper deals with the nature of this substance, which the author is led to regard as 4-cymol-2-indolindolignone [$\Delta^{2,2'}$-*indoxylcymol*] (annexed formula).



Commercial indoxylic acid was used as the starting point in place of indoxyl. This, when heated with glacial acetic acid until carbon dioxide ceased to be evolved, and then treated with thymol and a solution of ferric chloride in concentrated hydrochloric acid, gave a mixture of a blue, amorphous and a red, crystalline substance, of which only the latter gave a violet coloration with chloroform and aqueous hydrochloric acid. In subsequent experiments the indoxylic acid was decomposed by repeated extraction with boiling water; oxidation of the indoxyl contained in the filtrate then yielded the red substance; it forms prisms capped by pyramids, m. p. 218—220° (decomp.), and gives brownish-red solutions in the usual solvents which become violet on addition of hydrochloric acid. It is soluble in cold alkali hydroxides; hot sodium hydroxide decomposes it with formation of anthranilic acid, but the second product of fission could not be identified with certainty. Probably *p*-thymotinaldehyde is formed, and from this the above constitutional formula is deduced, and is further supported by the fact that the substance does not possess tinctorial power. The *hydrochloride*, brownish-black, microscopic needles, was analysed.

The sensitiveness of the author's method of detecting indican has been investigated; a distinct coloration is produced in the presence of 0·0032 mg. The method is thus about four times as sensitive as that of Obermayer.

For the colorimetric estimation of indican two methods are possible depending either on the use of the violet solution of the hydrochloride in chloroform, or on the hydrolysis of the salt in solution and the employment of the reddish-brown solution of the indolignone. Under definite conditions either method can be used, but the former is not always trustworthy, as it is sometimes difficult to exclude water completely from the chloroform solution, and thus to avoid intermediate shades. The following process is recommended: the indican solution (10 c.c.) is mixed with 5% thymol solution (1 c.c.) and fuming

hydrochloric acid containing 5 grams of ferric chloride per litre (10 c.c.). After two hours the solution is repeatedly extracted with chloroform (5 c.c. for each extraction) until a colourless solution is obtained. The combined chloroform extracts are shaken with water, treated with very dilute alkali (*N*/500—*N*/1000), united with a further portion of chloroform used for extracting the aqueous and alkaline solutions, and allowed to deposit any water. The colorimetric estimation is effected by comparison with standard solutions of 4-cymol-2-indolindolignone in chloroform. Control experiments show that the errors are rather greater in concentrated than in dilute solution; but that, in any case, the indican content of pure indican solutions can be determined in this manner. H. W.

Preparation of *N*-Anthraquinonylisatins. FARBENFABRIK VORM. F. BAYER & Co. (D.R.-P. 282490; from *J. Soc. Chem. Ind.*, 1915, **34**, 653).—Although acid chlorides such as benzoyl chloride, acetyl chloride, ethyl chloroformate, carbonyl chloride, etc., have no action on *N*-monoarylaminoanthraquinones, yet oxalyl chloride in the presence of condensing agents such as aluminium chloride, ferric chloride or phosphoric oxide gives characteristic products, namely, *N*-anthraquinonylisatins. G. F. M.

Acyl Compounds of *p*-Hydroxyphenylethylamine and β-Amino-4-ethylglyoxaline. F. HOFFMANN, LA ROCHE & Co. (D.R.-P. 281912; from *J. Soc. Chem. Ind.*, 1915, **34**, 735).—The amines are converted into aminoacylamines by treatment with a halogen acyl chloride followed by ammonia. *p*-Hydroxyphenylethylamine thus gives the fairly strongly basic *glycyl-p-hydroxyphenylethylamine*, and 4-β-aminoethylglyoxaline, *glycyl-4-β-aminoethylglyoxaline*, substances which are much less poisonous than the amines themselves. G. F. M.

***p*-Cyano- and *p*-Carboxy-Malachite Green.** BERTHOLD RASSOW and HERMANN GRUBER (*J. pr. Chem.*, 1915, [ii], **91**, 341—357).—Noelting and Gerlinger (A., 1906, i, 607) have shown that the introduction of various groups in the ortho-position of the unsubstituted benzene nucleus of malachite-green gives rise to dyes having a bluer shade than the parent substance, whilst in the para-position dyes of a yellower shade are produced; substitution in the meta-position has comparatively little influence on the colour.

The same effect is now found to accompany the introduction of the the cyano- and carboxyl groups.

4-*Cyano*-4′ : 4″-*tetramethyldiaminotriphenylmethane*,

$$CN\cdot C_6H_4\cdot CH(C_6H_4\cdot NMe_2)_2,$$

prepared by the gradual addition of phosphoryl chloride to a mixture of *p*-cyanobenzaldehyde and dimethylaniline with a little alcohol at 100°, forms yellow crystals, which become green and melt at 158—160°. It is oxidised by freshly-prepared, hydrated manganese peroxide and dilute sulphuric acid to 4-*cyano*-4′ : 4″-*tetramethyldiaminotriphenylcarbinol*, which crystallises with difficulty in nodular aggregates, m. p. 132°, simultaneously darkening, and gives rise to two series

of salts, one derived from the carbinol by combination with two equivalents of acid, the other from the corresponding dye-base with one equivalent of acid. The salts of the first series are formed only in the absence of water, and are readily converted by exposure to air into salts of the dye-base.

The *dihydrochloride* of the carbinol,

$$CN\cdot C_6H_4\cdot C(OH)(C_6H_4\cdot NMe_2,HCl)_2,$$

is obtained as a whitish-grey, amorphous powder by passing hydrogen chloride into a ethereal solution of the carbinol, and is transformed by solution in alcohol and exposure to air into the bronze-coloured *chloride* of the dye-base, $CN\cdot C_6H_4\cdot C(C_6H_4\cdot NMe_2):C_6H_4:NMe_2Cl$. The whitish-green *picrate* of the carbinol passes almost instantly into the *picrate* of the dye base, which forms a bronze-coloured, crystalline powder, m. p. 188—190°, and becomes green on exposure to air; the *oxalates* of the carbinol and dye-base, m. p. 172° (decomp.), are also described.

4′ : 4″-*Tetramethyldiaminotriphenylmethane-4-carboxylic acid*, prepared by hydrolysing the corresponding cyano-derivative with alcoholic potassium hydroxide, crystallises in small, white needles, m. p. 252°, with previous browning at 240°, yields a voluminous *potassium* salt and is oxidised by hydrated manganese peroxide and sulphuric acid to the *acid sulphate* of 4′ : 4″-*tetramethyldiaminotriphenylcarbinol-4-carboxylic acid*, $CO_2H\cdot C_6H_4\cdot C(C_6H_4\cdot NMe_2):C_6H_4:NMe_2\cdot O\cdot SO_3H$, which forms a bronze-coloured mass, and on treatment with aqueous potassium hydroxide is successfully converted into the bronze-coloured normal *sulphate*, $(C_{24}H_{25}O_2N_2)_2SO_4$, free *carbinol*,

$$CO_2H\cdot C_6H_4\cdot C(OH)(C_6H_4\cdot NMe_2)_2,$$

short, colourless needles, m. p. 268°, previously browning at 230°, and *potassium* salt of the carbinol, which forms a whitish-yellow, opalescent mass.

Both 4′ : 4″-tetramethyldiaminotriphenylcarbinol-4-carboxylic acid and its nitrile dye wool and mordanted cotton an intense yellowish-green.

Full details of improved methods for the preparation of *p*-cyanobenzaldehyde from *p*-aminobenzaldehyde by the diazo-reaction are also described. F. B.

Condensation of Acid Chlorides with the Ethyl Ester of (*a*) Cyanoacetic Acid, (*b*) Malonic Acid, and (*c*) Acetoacetic Acid. II. Some Experiments with Ethyl Phthaliminoacetoacetate and Ethyl γ-Ethoxyacetoacetate. JOHN BRADSHAW, HENRY STEPHEN, and CHARLES WEIZMANN (T., 1915, **107**, 803—813). —A continuation of previous work (T., 1913, **103**, 1855; compare Gabriel, A., 1913, i, 622; this vol., i, 409).

In addition to ethyl phthaliminoacetoacetate the condensation of phthaliminoacetyl chloride with ethyl sodiomalonate results in the formation of *ethyl bisphthaliminoacetylmalonate*,

$$(C_6H_4:C_2O_2:N\cdot CH_2\cdot CO)_2C(CO_2Et)_2,$$

small, white needles, m. p. 176°, the separation of which is effected by taking advantage of its sparing solubility in alcohol.

Both the ketonic and enolic forms of ethyl phthaliminoacetoacetate

react with phenylhydrazine, yielding 1-*phenyl*-3-*phthaliminomethyl*-5-*pyrazolone*, $C_6H_4{:}C_2O_2{:}N{\cdot}CH_2{\cdot}C\begin{matrix}CH_2\cdot CO\\ \diagup\!\!\diagdown\\ N\!-\!-\!NPh\end{matrix}$. This forms a fine crystalline powder, m. p. 192° (decomp.), and is hydrolysed by alcoholic potassium hydroxide to 1-*phenyl*-3-*phthalaminomethyl*-5-*pyrazolone*, a yellow, crystalline powder, m. p. 164° (decomp.).

Ethyl 1-*phenyl*-3-*phthaliminomethyl*-5-*pyrazolone*-4-*carboxylate*,

$$C_6H_4{:}C_2O_2{:}N{\cdot}CH_2{\cdot}C\begin{matrix}CH(CO_2Et)\cdot CO\\ \diagup\!\!\diagdown\\ N\!-\!-\!-\!-\!-\!-\!-\!-\!NPh\end{matrix},$$

prepared by heating ethyl phthaliminoacetylmalonate with phenylhydrazine in acetic acid solution, forms a pale yellow powder, m. p. 215°, and, on hydrolysis, yields the corresponding *phthalamino*-derivative (not isolated in a pure condition), which loses carbon dioxide at 120° with the formation of the phthalaminopyrazolone, m. p. 164°, described above. It is also produced by the action of phenylhydrazine on ethyl bisphthaliminoacetylmalonate, but is accompanied in this case by *phthaliminoacetylphenylhydrazide*, which forms needles, m. p. 199°, and has also been prepared by the interaction of phthaliminoacetyl chloride and phenylhydrazine in benzene solution.

The action of sodium nitrite on ethyl phthaliminoacetylmalonate and on the two forms of ethyl phthaliminoacetoacetate gives rise to *α-oximino-γ-phthaliminoacetone*, $C_6H_4{:}C_2O_2{:}NH{\cdot}CH_2{\cdot}CO{\cdot}CH{:}NOH$, prisms, m. p. 156° (decomp.). Attempts to reduce the latter compound to α-amino-γ-phthaliminoacetone were unsuccessful.

The behaviour of the phthalimino-derivatives of ethyl acetoacetate and ethyl acetomalonate on hydrolysis under various conditions has also been studied. The action of mineral acids results in the decomposition of the phthalimino-group, whilst alkalis give rise to the corresponding phthalamic acids. When the keto-form of ethyl phthaliminoacetoacetate is heated in a current of steam for half an hour, it undergoes partial transformation into the enolic form.

Under similar conditions the enol-form is converted into phthaliminoacetic acid and the substance, m. p. 110°, described by Gabriel and Coleman (A., 1909, i, 491 ; compare Pfaehler, A., 1913, i, 750).

If the distillation is continued for several hours, ethyl phthaliminoacetylmalonate and the ketonic form of ethyl phthaliminoacetoacetate yield phthaliminoacetone, whilst the enolic modification and ethyl bisphthaliminoacetylmalonate give rise to phthaliminoacetone and phthaliminoacetic acid.

Ethyl ethylidenebis-γ-ethoxyacetoacetate,

$$CHMe[CH(CO_2Et)\cdot CO\cdot CH_2\cdot OEt]_2,$$

prepared by the condensation of ethyl γ-ethoxyacetoacetate and acetaldehyde by means of diethylamine at 0°, forms needles, m. p. 96°, and is converted by boiling dilute sulphuric acid or hydrogen chloride in benzene solution into 1-*ethoxy*-4-*methyl*-2-*ethoxymethyl*cyclo*hexen*-6-*one*, $OEt{\cdot}CH_2{\cdot}C\begin{matrix}C(OEt)\!-\!-\!CO\\ \diagdown\!\!\diagup\\ CH_2\cdot CHMe\end{matrix}>CH_2$, a liquid, b. p. 157°/15 mm., having a pleasant terpene-like odour, and yielding a *semicarbazone*, plates, m. p. 232° (decomp.).

Methyl iodide reacts with the sodium derivative of ethyl γ-ethoxy-

acetoacetate in alcoholic solution, yielding ethyl γ-ethoxy-α-methylacetoacetate (compare Johnson, A., 1913, i, 587). The corresponding ethyl, b. p. 124°/15 mm., *propyl*, b. p. 137°/18 mm., iso*propyl*, b. p. 131°/18 mm., and iso*butyl*, b. p. 128°/10 mm., derivatives were prepared in a similar manner. The methyl and ethyl derivatives were submitted to hydrolysis under various conditions in order to obtain the corresponding ketones, but only small yields were obtained owing to "acid" hydrolysis simultaneously taking place; with the other alkyl derivatives the "acid" hydrolysis chiefly occurs.

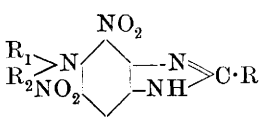
2-*Ethoxymethylquinoxaline*, a pale yellow liquid, b. p. 237°/760 mm. or 144°/18 mm., $C_6H_4<^{N:C\cdot CH_2\cdot OEt}_{N:CH}$, prepared by heating α-oximino-γ-ethoxyacetone and *o*-phenylenediamine in dilute acetic acid solution, forms a *platinichloride*, decomp. 250°, *picrate*, m. p. 216°, and is oxidised by alkaline potassium permanganate to *pyrazine*-2 : 5 : 6-*tricarboxylic acid*, silky needles, m. p. 191° (decomp.), which yields a green, crystalline *copper* salt. The preparation of ethoxyacetamide (Sommelet, A., 1907, i, 21) from the acid chloride is also described. F. B.

Preparation of Amino-derivatives of Substituted Benziminazoles. D. Maron (D.R.-P. 282374; from *J. Soc. Chem. Ind.*, 1915, **34**, 652).—Benziminazoles of the type

$$(5)X\cdot C_6H_3<^{-N(3)}_{NH(1)}>C\cdot R(2),$$

where X = an alkyl, halogen or oxyalkyl group, and R = a hydrogen, alkyl, hydroxyl or amino-group, when treated with concentrated sulphuric acid and nitrates yield 4 : 6-dinitro-compounds, which are entirely or partly reduced to diamines or nitroamines, substances which are important intermediate products for the preparation of dyes. G. F. M.

Preparation of Basic Condensation Products of the Benziminazole Series. D. Maron (D.R.-P. 282375; from *J. Soc. Chem. Ind.*, 1915, **34**, 652—653). — 5-Halogen-4 : 6-dinitrobenziminazoles (preceding abstract) are condensed with primary or secondary aliphatic amines or primary aromatic amines or their substitution products to give compounds of the annexed formula which may be used in the preparation of dyes or pharmaceutical products (R = hydrogen, alkyl, OH, or NH_2; R_1 = alkyl, phenyl, $\cdot C_6H_4\cdot OH$, $\cdot C_6H_4\cdot CO_2H$, $\cdot C_6H_4\cdot NH_2$, $(C_6H_4S)_2$, or $C_6H_4\cdot SO_3H$; and R_2 = hydrogen or alkyl, where R_1 is also alkyl). G. F. M.



Derivatives of 2-Pyridylhydrazine and 2-Quinolylhydrazine. Robert George Fargher and Reginald Furness (T., 1915, **107**, 688—699).— A large number of derivatives of the above-named hydrazines have been prepared, but all attempts to convert them into pyrindole and quinindole derivatives by the action of zinc chloride, hydrochloric acid, and other condensing agents were unsuccessful (compare Perkin and Robinson, T., 1913, **103**, 1974).

2-*Pyridylhydrazine*, $C_5H_4N\cdot NH\cdot NH_2$, prepared by heating 2-chloropyridine with hydrazine hydrate, has m. p. about 46°, b. p. 185°/140 mm. or 140°/20 mm., forms a *picrate*, slender needles, m. p. 160—161° (decomp.), *platinichloride*, m. p. 256° (decomp.) with previous blackening at 160°, and reacts with the following compounds, yielding the corresponding 2-*pyridylhydrazones*; *acetaldehyde*, needles, m. p. 70°; *benzaldehyde*, long, glistening, colourless needles, m. p. 148°; *acetone*, rhombic prisms, m. p. 73°, b. p. 145°/25 mm. or 180°/70 mm.; *acetophenone*, m. p. 90°; *pyruvic acid*, $C_8H_9O_2N_3,1\frac{1}{2}H_2O$, m. p. 188°, evolving carbon dioxide; *ethyl pyruvate*, slender needles containing $1H_2O$ and having m. p. 53°, or in the anhydrous condition, m. p. 74°. It forms an *acetyl* derivative, twin prisms, m. p. 150°, *semicarbazide*,

$$C_5H_4N\cdot NH\cdot NH\cdot CO\cdot NH_2,$$

m. p. 186°, and reacts with phthalic anhydride in boiling alcoholic solution, yielding *phthalyl-2-pyridylhydrazide*,

$$\begin{matrix} C_6H_4 \\ | \\ CO\cdot O \end{matrix}\!\!>\!C{:}N\cdot NH\cdot C_5H_4N,$$

colourless, rhombic prisms, m. p. 208°.

With ethyl acetoacetate it forms a hydrazone which is converted by distillation under diminished pressure into 1-(2′-*pyridyl*)-3-*methyl*-5-*pyrazolone*, $\begin{matrix} CH_2\cdot CO \\ | \\ CMe{=}N \end{matrix}\!\!>\!N\cdot C_5H_4N$, m. p. 110°.

On treatment with sodium nitrite in cold dilute acetic acid solution it yields 1 : 2 : 3 : 9-*benzoisotetrazole*, $C_5H_4N\!<\!\begin{matrix} N \\ N \end{matrix}\!>\!N$, colourless, elongated prisms, m. p. 159°.

1 : 2 : 9-*Benzoisotriazole*, $C_5H_4N\!<\!\begin{matrix} N{-}{-} \\ CH \end{matrix}\!>\!N$, prepared by heating 2-pyridylhydrazine with formic acid, forms a very hygroscopic, white, crystalline mass and yields a *platinichloride*, which does not melt at 300°, and an explosive additive *compound* with silver nitrate,

$$C_6H_5N_3,AgNO_3,$$

slender needles, decomp. 228°.

s-2-*Pyridyl*-2-*quinolylhydrazine*, $C_9H_6N\cdot NH\cdot NH\cdot C_5H_4N$, obtained by the interaction of 2-chloroquinoline and 2-pyridylhydrazine, either alone or in the presence of pyridine, has m. p. 177°.

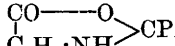
The 2-*quinolylhydrazones* of the following compounds are also described: *acetaldehyde*, slender, colourless, silky needles, m. p. 151°; *acetophenone*, yellow needles, m. p. 122°; *pyruvic acid*, decomp. 200° with previous darkening at 170°; *ethyl pyruvate*, m. p. 134°; *laevulic acid*, m. p. 200° (decomp.); *ethyl acetoacetate*, which forms colourless needles, m. p. 90°, and is converted by heating on the water bath into 1-(2′-*quinolyl*)-3-*methyl*-5-*pyrazolone*, voluminous mass of fluffy needles, m. p. 140°.

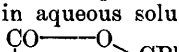
2-Quinolylhydrazine yields an *acetyl* derivative, clusters of elongated, rhombic prisms, m. p. 195°, *benzoyl* derivative, colourless needles, m. p. 204°, and reacts with succinic and phthalic anhydrides in alcoholic solution, yielding respectively *succinyl*-2-*quinolylhydrazide*,

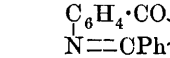
$$\begin{matrix} CO{-}{-}O \\ | \\ CH_2\cdot CH_2 \end{matrix}\!\!>\!C{:}N\cdot NH\cdot C_9H_6N,$$

pale yellow rhombs, m. p. 160°, and *phthalyl-2-quinolylhydrazide*, pale orange plates, m. p. 236°. F. B.

Anthranil. IX. Constitution of Acylanthranils. GUSTAV HELLER (*Ber.*, 1915, **48**, 1183—1195).—Benzoylanthranil reacts with hydrazine hydrate in alcoholic solution at the ordinary temperature, yielding *3-hydrazino-3-phenyl-3 : 4-dihydrobenzoxazone*,



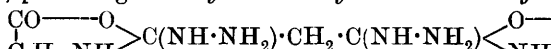
colourless needles, m. p. 187—188° (decomp.), which is converted by nitrous acid in aqueous solution into *3-azimido-3-phenyl-3 : 4-dihydrobenzoxazone*,  , colourless needles, m. p. 111—112°; this when heated with dilute sodium hydroxide solution gives benzoylanthranilic acid. The hydrazine compound when heated with alkali or acetic acid passes into *3-amino-2-phenyl-4-quinazolone*,



colourless needles, m. p. 178—179°.

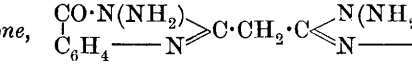
In a similar manner to the above, acetylanthranil reacts with hydrazine hydrate, giving *3-hydrazino-3-methyl-3 : 4-dihydrobenzoxazone* colourless needles, m. p. 148°, which is converted by acetic acid into the 3-amino-2-methyl-4-quinazolone already described (Bogert and Gortner, A., 1909, i, 679).

Malonylbisanthranilic acid (von Pollack, A., 1905, i, 353) is converted by boiling acetic acid into *malonylbisanthranil*, yellow needles, m. p. 242° (decomp.), which reacts with hydrazine hydrate in alcoholic solution, producing *3-methylene-bis-3-hydrazino-3 : 4-dihydrobenzoxazone*,

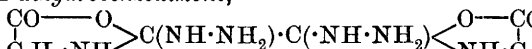


unfused at 295°; this dissolves in hot sodium carbonate solution, and on acidification *malonylbisanthranilic acid bis-hydrazone*,

$CO_2H \cdot C_6H_4 \cdot NH \cdot C(:N \cdot NH_2) \cdot CH_2 \cdot C(:N \cdot NH_2) \cdot NH \cdot C_6H_4 \cdot CO_2H$,

m. p. 295° (decomp.), separates. In hot acetic acid solution 3-methylene-bis-3-hydrazino-3 : 4-dihydrobenzoxazone passes into *2-methylene-bis-3-amino-4-quinazolone*,  , pale yellow needles, unfused at 300°.

Oxalylbisanthranil (Bogert and Gortner, A., 1910, i, 283) in a similar manner is convertible by hydrazine hydrate into *3-bis-3-hydrazino-3 : 4-dihydrobenzoxazone*,

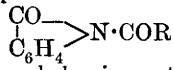


m. p. 219—220° (decomp.), which by successive treatment with sodium hydroxide solution and acetic acid undergoes conversion into *oxalyl-bis-anthranilic acid bishydrazone*,

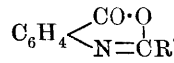
$CO_2H \cdot C_6H_4 \cdot NH \cdot C(:N \cdot NH_2) \cdot C(:N \cdot NH_2) \cdot NH \cdot C_6H_4 \cdot CO_2H$,

yellow needles, m. p. 177—178°

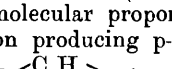
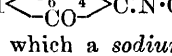
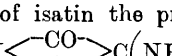
These reactions are interpreted as in favour of the formula



for the acylanthranils, the behaviour towards hydrazine hydrate especially being difficult to reconcile with the alternative formula



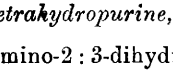
D. F. T.

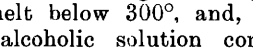
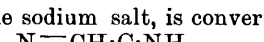
Isatin. A. Binz and R. Hueter (*Ber.*, 1915, **48**, 1038—1041).—Isatin reacts with an equimolecular proportion of *p*-phenylenediamine in aqueous-alcoholic solution producing p-*aminophenylimesatin* (*isatin*-3-p-*aminophenylimide*),  , red needles, m. p. 239—241° (decomp.), from which a *sodium* salt and a *silver* salt were prepared; with an excess of isatin the product is *di*-(p-*aminophenylimesatyl*)-*imesatin*,  , yellowish-red scales, m. p. 310° (decomp.); this compound has already been prepared by Möhlau and Litter (A., 1906, i, 612), but was incorrectly described as *p*-aminophenylimesatin. *p*-Aminophenylimesatin when warmed with acetic acid undergoes conversion into di-(*p*-aminophenylimesatyl)-imesatin, the change presumably being preceded by partial fission; it also condenses with benzaldehyde, giving a *benzylidene* derivative, and when oxidised with hydrogen peroxide gives a substance, $C_{14}H_{11}O_2N_3$, possibly *aminophenylisatoic anhydride*,  , needles, m. p. 232°.

When heated with *p*-phenylenediamine in aqueous alcoholic solution, dibromoisatin is converted into p-*aminophenyldibromo-imesatin*, reddish-violet crystals, m. p. above 300°. D. F. T.

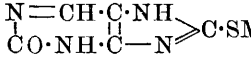
Preparation of a Pyrazolone Derivative. I. Abelin, E. Bürgi, and M. Perelstein (D.R.-P. 282264; from *J. Soc. Chem. Ind.*, 1915, **34**, 686). — 4-Dimethylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone gives with the ω-methylsulphonate of the *p*-aminophenyl ester of salicylic acid a compound, $C_{27}H_{30}O_7N_4S$, which is strongly antiseptic and disinfecting, and is more effective as an anæsthetic and narcotic, but less toxic than the original pyrazolone. G. F. M.

Purines. XVII. A New Synthesis of Alkylaminopurines. 2-Oxy-8-thiopurine, 2-Oxy-8-methylmercaptopurine, 2-Oxy-8-methylaminopurine, and 2-Oxy-6 : 9-dimethyl 8-thiopurine. Carl O. Johns (*J. Biol. Chem.*, 1915, **21**, 319—323. Compare this vol., i, 179).—Methylaminopurines may be prepared from thiopurines by the action of methyl iodide on their sodium salts, and subsequent treatment of the resulting methylthiolpurines with methylamine, the methylthiol group being removed as methyl mercaptan. The present paper deals with the conversion of 2-oxy-8-thio-2 : 3 : 8 : 9-tetrahydropurine into 2-oxy-8-methylamino-2 : 3-dihydropurine.

2-*Oxy*-8-*thio*-2 : 3 : 8 : 9-*tetrahydropurine*,  , prepared by heating 5 : 6-diamino-2 : 3-dihydro-2-pyrimidone with thio-

carbamide at 180—185°, forms globular aggregations of very minute prisms, does not melt below 300°, and, when heated with methyl iodide in aqueous alcoholic solution containing sufficient sodium ethoxide to form the sodium salt, is converted into *2-oxy-8-methylthiol-2 : 3-dihydropurine*,  , which crystallises in slender prisms, decomposes slowly above 260°, and is transformed by heating with aqueous methylamine at 100° into *2-oxy-8-methylamino-2 : 3-dihydropurine*,  , sheaf-like bundles of minute crystals, which do not melt below 300°.

2-Oxy-8-thio-6 : 9-dimethyl-2 : 3 : 8 : 9-tetrahydropurine,



prepared from 5-amino-4-methylamino-6-methyl-2 : 3-dihydro-2-pyrimidone and thiocarbamide at 170—180°, forms a light-coloured powder.

It is also mentioned that 2-oxy-8-methylthiol-2 : 3-dihydropurine reacts with ammonia at a high temperature, but the resulting 2-oxy-8-amino-2 : 3-dihydropurine has not yet been isolated in a pure condition. F. B.

Preparation of Mercurous Salts of Basic Purines. L. Rosenthaler and A. Abelmann (D.R.-P. 282376; from *J. Soc. Chem. Ind.*, 1915, **34**, 686).—Mercurous salts of basic purines, such as caffeine, theobromine and theophylline, are prepared by allowing the latter to react in dilute nitric acid solution with an aqueous solution of mercurous nitrate. These salts are of interest, since purines have been shown to prevent the harmful effect of mercury compounds. G. F. M.

Preparation of Mercury Compounds of Basic Purines. L. Rosenthaler and A. Abelmann (D.R.-P. 282377; from *J. Soc. Chem. Ind.*, 1915, **34**, 686).—When acid solutions of theobromine or theophylline are treated with mercuric acetate, or an aqueous suspension of theobromine or theophylline is warmed with mercuric oxide in presence or absence of alkalis, stable compounds are formed which do not give the usual reactions of mercuric salts, and in which the mercury is combined in another form to that in the known *N*-mercury trioxypurines. The theobromine compound is prepared with freshly prepared mercuric oxide in the dark, the excess of theobromine being extracted with chloroform. G. F. M.

Some Derivatives of Carbamide. M. Scholtz (*Arch. Pharm.*, 1915, **253**, 111—117).—A number of condensations of ketones with carbamide, at higher temperatures than usual, are described.

When equal weights of acetophenone and carbamide are heated at 170° for two or three hours, *di-α-phenylethylidenecarbamide*,

$$CPhMe{:}N{\cdot}CO{\cdot}N{:}CPhMe,$$

is formed, in colourless prisms, m. p. 176° *Di-α-phenylpropylidenecarbamide*, $C_{19}H_{20}ON_2$, is obtained in the same way, in colourless rods, m. p. 196—197°. These compounds are stable towards alcoholic potassium hydroxide, and are only slowly hydrolysed by alcoholic

hydrogen chloride. Benzophenone does not react so readily, for the molten substances do not mix, and the product is *diphenylmethylenebiuret*, $CPh_2{:}N{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$, needles, decomp. above 300°.

Equal weights of ethyl acetoacetate and carbamide at 170° yield *β-dicarbamidobutyrylcarbamide*,

$$(NH_2{\cdot}CO{\cdot}NH)_2CMe{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

a white, granular substance which softens above 130°, and has m. p. 170°. When heated at 200°, it loses ammonia and forms 4 : 6-*diketo*-2-*methylhexahydro*-1 : 3 : 5-*triazine*-2-*acetylcarbamide*,

$$NH\langle{}^{CO{\cdot}NH}_{CO{\cdot}NH}\rangle CMe{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

a crystalline powder with no definite m. p. Similarly, ethyl benzoylacetate yields a small quantity of phenyluracil, removed by boiling water, but chiefly *ββ-dicarbamido-β-phenylpropionylcarbamide*,

$$(NH_2{\cdot}CO{\cdot}NH)_2CPh{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

m. p. 213°, which, when heated at 250°, changes into 4 : 6-*diketo*-2-*phenylhexahydro*-1 : 3 : 5-*triazine*-2-*acetylcarbamide*, $C_{12}H_{13}O_4N_5$, m. p. 260°.

J. C. W.

Decompositions of Certain Nitrogen Compounds. A. Angeli (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 1093—1098).—Unsuccessful attempts have been made by various investigators to isolate di-imide, which undergoes immediate decomposition in one of the following methods, according to the experimental conditions:

$2NH{:}NH = N_2 + N_2H_4$, $2NH{:}NH = N_3H + NH_3$ or $NH{:}NH = N_2 + H_2$.

Further, the author has shown (A., 1909, i, 421) that benzenesulphonyl phenylhydrazine, when treated with alkali, loses benzenesulphinic acid, the phenyldi-imide thus liberated reacting immediately with benzaldehyde, for instance: $NPh{:}NH + Ph{\cdot}CHO = NHPh{\cdot}NHBz$; if, however, benzaldehyde is absent and the liquid is shaken with ether, the phenyldi-imide reacts with the original compound, yielding phenylhydrazine and benzenediazosulphone: $Ph{\cdot}SO_2{\cdot}NH{\cdot}NHPh + NPh{:}NH = NPh{:}N{\cdot}SO_2Ph + NHPh{\cdot}NH_2$.

A similar reaction might be expected with the diphenyldisulphonehydrazine, $SO_2Ph{\cdot}NH{\cdot}NH{\cdot}SO_2Ph$, obtained by Hinsberg (A., 1894, i, 290), who found that it forms a potassium salt giving benzenesulphinic acid and nitrogen when heated. This reaction probably takes place with intermediate formation of dihydroxyhydrazine, which decomposes thus: $OH{\cdot}NH{\cdot}NH{\cdot}OH = N_2 + 2H_2O$; the final reaction would then be expressed by the equation, $SO_2Ph{\cdot}NH{\cdot}NH{\cdot}SO_2Ph = N_2 + 2Ph{\cdot}SO_2H$. The reaction may, however, be gradual, and give rise firstly to the compound, $OH{\cdot}NH{\cdot}NH{\cdot}SO_2Ph$, this losing another molecule of benzenesulphinic acid and forming nitrogen and water, under the further action of alkali. That such an intermediate compound is formed is supported by the fact that the action of nitrosobenzene on diphenyldisulphonehydrazine in presence of alkali yields the *compound*, $Ph{\cdot}SO_2{\cdot}NH{\cdot}N{:}NPh{:}O$, which forms shining, colourless needles, decomposing suddenly at 102°, and explodes violently on heating or percussion. This compound has an acid character, its salts being probably derived from the tautomeric form,

$$Ph{\cdot}SO(OH){:}N{\cdot}N{:}NPh{:}O.$$

With ferric and copper salts, it furnishes complexes closely resembling those given by nitrosophenylhydroxylamine (cupferron). The further action of alkali results in the loss of the second molecule of benzenesulphinic acid, with probable formation of phenylazide oxide, this undergoing ready decomposition into nitrosobenzene and nitrogen,

$$O{:}NPh{:}N{:}N = Ph{\cdot}NO + N_2.$$

T. H. P.

Tetra-arylhydrazines. J. SUREDA BLANES (*Anal. Fis. Quim.*, 1915, **13**, 293—298).—*Diacetylaminotetraphenylhydrazine*, formed by oxidation of *p*-acetylaminodiphenylamine in acetone solution with permanganate, forms white crystals which melt with decomposition between 100° and 124°. It gives an intense violet coloration with acetic acid, and a blue coloration with sulphuric and hydrochloric acid respectively. A. J. W.

Ditertiary Hydrazines, XIX. A New Contribution to the Knowledge of Bivalent Nitrogen. HEINRICH WIELAND (*Ber.*, 1915, **48**, 1078—1096).—It has already been shown that the tendency of tetra-arylhydrazines towards dissociation depends on the nature of the aryl radicles present, negative substituents like the nitro-group militating against such dissociation, whilst the methyl and especially the methoxyl radicles facilitate the change. Thus with tetra-anisylhydrazine (Wieland and Lecher, A., 1912, i, 907; Wieland and Müller, A., 1913, i, 1320) the colourless base gives green solutions, the colour being due to the presence of the free radicle $\cdot N(C_6H_4{\cdot}OMe)_2$.

Tetra-p-*dimethylaminotetraphenylhydrazine*,

$$(NMe_2{\cdot}C_6H_4)_2N{\cdot}N(C_6H_4{\cdot}NMe_2)_2$$

has now been obtained by the oxidation of *p*-tetramethyldiaminodiphenylamine in ethereal pyridine solution by silver oxide in the presence of sodium sulphate at −15°, and is found to form colourless, microscopic rods, m. p. 74—76°, which are rapidly turned blue by moisture. The hydrazine compound gives intensely yellow solutions in solvents such as ether, acetone, and pyridine, the colour being due to dissociation, the occurrence of which can be demonstrated by molecular weight determination. In light petroleum, a colourless solution is obtained, but a yellow colour develops on warming. It is found that in benzene solution approximately 10% and in nitrobenzene approximately 21% of the hydrazine compound is present in the form of single radicles $\cdot N(C_6H_4{\cdot}NMe_2)_2$, the phenomenon therefore being much more marked than in the analogous case of hexaphenylethane and triphenylmethyl.

Tetradimethylaminotetraphenylhydrazine exhibits many of the reactions characteristic of its "dissociated" nature; it immediately unites with nitric oxide, forming *tetramethyldiaminodiphenylnitrosoamine*, $NO{\cdot}N(C_6H_4{\cdot}NMe_2)_2$, yellow needles, m. p. 155° (decomp.), and combines with triphenylmethyl in benzene solution in an atmosphere of carbon dioxide, giving *tetramethyldiaminodiphenyltriphenylmethylamine*, $CPh_3{\cdot}N(C_6H_4{\cdot}NMe_2)_2$, wedge-shaped crystals, m. p. 157°, with reddening which commences at 120°. Solutions of the tetradimethylaminotetraphenylhydrazine on account of the bivalent nitrogen radicle

present are unstable to light and gradually become red, the colour being due to the formation of *trimethylindamine* (*dimethylaminophenylmethylquinonedi-imide*), $NMe{:}C_6H_4{:}N{\cdot}C_6H_4{\cdot}NMe_2$, the mechanism of the change being uncertain; the hydrazine compound also undergoes concurrent decomposition in the manner observed previously with analogous substances, giving tetradimethylaminodiphenylamine,

$$NH(C_6H_4{\cdot}NMe_2)_2,$$

and *tetramethyldiaminotetramethyldiaminodiphenyldihydrophenazine*,

$$NMe_2{\cdot}C_6H_3\begin{<}N(C_6H_4{\cdot}NMe_2)\\N(C_6H_4{\cdot}NMe_2)\end{>}C_6H_3{\cdot}NMe_2,$$

a yellow powder, the colourless solution of which in acids is turned blue by the action of oxidising agents, such as ferric chloride or bromine. Oxidation of the hydrazine compound in ethereal solution by silver oxide gives rise to the above-mentioned trimethylindamine compound, the presence of which is most readily detected by shaking the solution with nitric oxide, when the *dinitrosoamine*

$$NO{\cdot}NMe{\cdot}C_6H_4{\cdot}N(NO){\cdot}C_6H_4{\cdot}NMe_2$$

is obtained.

Tetradimethylaminotetraphenylhydrazine is exceedingly sensitive to moisture, two molecules of the base yielding tetramethyldiaminodiphenylamine, $NH(C_6H_4{\cdot}NMe_2)_2$, and the colour base,

$$OH{\cdot}NMe_2{:}C_6H_4{:}N{\cdot}C_6H_4{\cdot}NMe_2,$$

of Bindschedler's green, the latter compound undergoing rapid decomposition into Phenol-blue, $O{:}C_6H_4{:}N{\cdot}C_6H_4{\cdot}NMe_2$, and dimethylamine, especially in the presence of alkalis. This effect of water in producing a green coloration which passes to blue on the addition of an alkali provides a decisive test for the hydrazine compound, but that the effect is in reality due to the free diarylnitrogen radicle is shown by the fact that a benzene solution decolorised by the addition of a five-fold volume of light petroleum is hardly affected by shaking with water, whereas a solution similarly diluted with benzene rapidly gives a green coloration with water.

None of the tetra-arylhydrazines investigated hitherto have possessed any marked basic nature, giving no salts with dilute acids, although coloured additive quinonoid compounds were obtainable with mineral acids and acetic acid in the absence of water (Wieland, A., 1907, i, 1076). Tetradimethylaminotetraphenylhydrazine on account of the presence of the amino-groups forms colourless salts of normal type, and it is noteworthy that the change in the valency of the amino-nitrogen atoms causes a strengthening in the mutual attachment of the nitrogen atoms in the hydrazine nucleus, the $:N{\cdot}N:$ linking being reducible much more readily in the free hydrazine base than in its salts.

p-Tetramethyldiaminodiphenylamine, $NH(C_6H_4{\cdot}NMe_2)_2$, when pure is a colourless solid, m. p. 121°, and is best produced by reduction of Bindschedler's green (*Ber.*, 1883, **16**, 866) with sodium hyposulphite; when oxidised in ethereal solution in the presence of alkalis by potassium ferricyanide it yields Phenol-blue and dimethylamine, whereas in the presence of sodium hydrogen carbonate the product is the ferrocyanide of Bindschedler's colour base. On the other hand, on oxidation in ethereal solution with such agents as silver oxide

or lead dioxide the product is the trimethylindamine already mentioned above, accompanied by a considerable quantity of tetradimethylaminotetraphenylhydrazine, the presence of the latter substance being demonstrable by the formation of tetramethyldiaminodiphenylnitrosoamine (see above) on treatment with nitric oxide; the tetramethyldiaminodiphenylamine gives no nitrosoamine under these conditions.

D. F. T.

The Intermediate Occurrence of Free Radicles in Chemical Reactions. The Decomposition of Aromatic Hydrazo-compounds. HEINRICH WIELAND (*Ber.*, 1915, **48**, 1098—1112).—The intermediate occurrence of free radicles is frequently postulated in the explanation of the mechanism of various reactions, such as the synthesis of ethane by the action of sodium on methyl iodide, but the assumption is not necessarily a correct one (compare Acree, A., 1903, i, 724). The analogous assumption in the case of the benzidine rearrangement and in the transformation of the diarylnitrosoamines into *p*-nitrosodiarylamines is also not representative of the facts because the free $\cdot NPh_2$ radicles to which tetraphenylhydrazine can give rise (see Wieland, preceding abstract) do not condense to form diphenylbenzidine and do not combine with nitric oxide with production of *p*-nitrosodiphenylamine.

The decomposition of hydrazobenzene and other symmetrical diarylhydrazines according to the equation $2NHR\cdot NHR = NR{:}NR + 2NH_2R$ (Stieglitz and Curme, A., 1913, ii, 398; Curme, 1913, ii, 854) also has been explained by the primary formation of aniline and the free radicle :NR. A more natural hypothesis is that by elimination of the hydrogen from one molecule of the diarylhydrazine, the azo-compound is produced, whilst the nascent hydrogen atoms reduce a second molecule to the corresponding amino-compound; this view receives confirmation from the fact that palladium black induces the conversion of hydrazobenzene into azobenzene and aniline in benzene solution even at the ordinary temperature, and that a part of the hydrogen becomes occluded by the metal (Wieland, A., 1912, i, 247).

As has been demonstrated by Stieglitz and Curme, the decomposition of these diarylhydrazines is a unimolecular reaction, but the measurable reaction is not of necessity the change $NHR\cdot NHR \longrightarrow NH_2R + NR$ followed by a rapid coupling of the :NR radicles, because a measurable reaction, $NHR\cdot NHR \longrightarrow NR{:}NR + 2H$, followed by a rapid reduction, $NHR\cdot NHR + 2H = 2NH_2R$, would give the same unimolecular effect. It is possible to distinguish between these two alternatives by submitting an unsymmetrical diarylhydrazine, NHR·NHR′, to the decomposition, for in such a case the NR and NR′ radicles assumed in the former explanation will be capable of condensing to give the azo-compounds N_2R_2, N_2R_2', and NR:NR′; also, in the former view of the reaction, the amines NH_2R and NH_2R' need not be produced in equimolecular proportion. On the other hand, if the second version is correct, only the mixed azo-compound will be produced, and the two amines should be formed in equivalent amounts.

p-Methylhydrazobenzene, the behaviour of which had already been examined by Curme, has been re-investigated from this point of view.

After heating in alcoholic solution at 132° for ten hours, the reaction product contained aniline, toluidine, *p*-methylazobenzene, and a little semidine. Contrary to the earlier result, the two former bases which were separated from solution as the oxalates were formed in equimolecular quantity, as determined by the bromination method (Curme, *loc. cit.*).

[With A. REVERDY and B. HEINEMANN.]—In a similar manner p-*tolyl*-p-*anisylhydrazine*, $OMe\cdot C_6H_4\cdot NH\cdot NH\cdot C_6H_4Me$, colourless needles, m. p. 95°, obtained by reduction of *tolueneazoanisole*,

$$OMe\cdot C_6H_4\cdot N{:}N\cdot C_6H_4Me,$$

orange-yellow prisms, m. p. 110—111°, with zinc dust and ammonia, underwent decomposition in alcohol at 144°, giving tolueneazoanisole as the only azo-compound, accompanied by *p*-toluidine and *p*-anisidine in equivalent proportions. The tolueneazoanisole required for this investigation was prepared by condensation of *p*-nitrosotoluene and *p*-anisidine in boiling alcohol containing a little acetic acid.

[With B. HEINEMANN.]—*p*-Chlorobenzeneazo-*p*-toluene,

$$C_6H_4Cl\cdot N{:}N\cdot C_6H_4Me,$$

was prepared by condensation of nitrosotoluene with *p*-chloroaniline; it forms orange-yellow leaflets, m. p. 153°, and is probably identical with the compound obtained by Paganini (A., 1891, 556) by the action of phosphorus pentachloride on *p*-hydroxybenzeneazo-*p*-chlorobenzene. Reduction by zinc dust and ammonia converted it into s-p-*chlorophenyl*-p-*tolylhydrazine*, $C_6H_4Cl\cdot NH\cdot NH\cdot C_6H_4Me$, needles, m. p. 124°. Decomposition of this compound in alcoholic solution at 144° gave *p*-chlorobenzeneazo-*p*-toluene, together with a semidine, probably 4-chloro-2′-aminodiphenylamine, needles, m. p. 130°, *p*-toluidine and *p*-chloroaniline, the two latter bases being in equivalent proportions.

[With A. REVERDY.]—Ethyl *p*-aminobenzoate condenses with nitrosobenzene in hot alcoholic solution containing acetic acid, with formation of ethyl benzeneazo-*p*-benzoate, m. p. 86—87°, which on reduction with zinc dust and ammonia is converted into *ethyl benzenehydrazo*-p-*benzoate*, $NHPh\cdot NH\cdot C_6H_4\cdot CO_2Et$, m. p. 110°. This decomposed in xylene solution at 160—170°, the only azo-compound in the product being ethyl benzeneazo-*p*-benzoate.

The experimental evidence is therefore entirely against the transient existence of free radicles of the type NR during the decomposition of these *s*-diarylhydrazines, and the results provide strong confirmation of the view that the first stage of the decomposition is the formation of the corresponding azo-compound and hydrogen, the latter effecting the reduction of a second molecule of the hydrazine compound.

D. F. T.

Aromatic Hydrazines. XX. The Dissociation of Triphenylhydrazine. HEINRICH WIELAND and ARNO REVERDY (*Ber.*, 1915, **48**, 1112—1116).—The tetra-aryl hydrazines are known to undergo partial dissociation into free NR_2 radicles already at the ordinary temperature and the diaryldialkylhydrazines, such as diphenyldimethylhydrazine (Wieland and Fressel, A., 1912, i, 903), have also been shown to undergo distinct dissociation at 135°. As hydrazobenzene gives no indication of such dissociation, the examination of triphenylhydrazine

appeared to be of interest, especially as in this case there are two possible methods of dissociation, namely, into two free radicles, NPh_2, and NHPh, or into diphenylamine and the radicle NPh; the latter course would be analogous to that suggested by Stieglitz and Curme in connexion with the decomposition of hydrazobenzene (compare, however, preceding abstract).

Triphenylhydrazine (Busch and Hobein, A., 1907, i, 552) is conveniently prepared by the action of magnesium phenyl bromide on diphenylnitrosoamine (see Wieland and Roseeu, this vol., i, 797). When heated in boiling xylene under an atmosphere of carbon dioxide, it undergoes decomposition, giving diphenylamine and azobenzene together with quinone-anildiphenylhydrazone, $NPh{:}C_6H_4{:}N{\cdot}NPh_2$, which was identified by its reduction to diphenylamine and *p*-aminodiphenylamine (Wieland and Wecker, A., 1911, i, 82). The formation of these substances accords well with the second of the above possibilities; the NPh radicle couples to azobenzene and also condenses with unaltered triphenylhydrazine, giving a compound of the formula

$$NHPh{\cdot}C_6H_4{\cdot}NH{\cdot}NPh_2,$$

which by scission of hydrogen produces quinoneanildiphenylhydrazone; the nascent hydrogen disappears by reducing unaltered triphenylhydrazine to diphenylamine and aniline, the presence of the last substance having also been proved.

In a similar manner, *phenyldi*-p-*tolylhydrazine*, $NHPh{\cdot}N(C_6H_4Me)_2$, was prepared by treating di-*p*-tolylnitrosoamine with magnesium phenyl bromide in ethereal solution. The product, colourless needles, m. p. 142—143° with incipient formation of a brown coloration at 120°, decomposes in xylene solution, giving azobenzene, aniline, di-*p*-tolylamine and a reddish-brown substance, which was recognised by its reduction products to be quinone-anildi-*p*-tolylhydrazone. The behaviour of this ditolylphenylhydrazine on decomposition is therefore quite analogous to that of triphenylhydrazine. D. F. T.

Diphenylmethenylhydrazidine (Phenyliminophenylhydrazinomethane). M. Busch and Wilh. Dietz (*J. pr. Chem.*, 1915, [ii], **91**, 325—329. Compare A., 1911, i, 86; 1914, i, 584).—In view of the widely different values given in the literature for the melting point of diphenylmethenylhydrazidine (Zwingenberger and Walther, A., 1898, i, 520; Dains, A., 1902, i, 602; Schmidt, A., 1903, i, 681), the authors were of the opinion that the compound existed in two isomeric forms: (I.) $NH_2{\cdot}NPh{\cdot}CH{:}NPh$ and (II.) $NHPh{\cdot}NH{\cdot}CH{:}NPh$. A repetition of the various methods of preparation has shown, however, that only one form crystallising in colourless leaflets, m. p. 109·5°, is produced.

That the hydrazidine has the constitution represented in (II) has been proved (1) by its oxidation with mercuric oxide in benzene solution at the ordinary temperature to benzeneazomethaneanil,

$$NPh{:}N{\cdot}CH{:}NPh,$$

and (2) by its formation from α-formylphenylhydrazine and aniline by heating with phosphoric oxide in benzene solution.

Benzeneazomethaneanil crystallises in radiating clusters of red needles, m. p. 62—63°, which rapidly decompose in alcoholic solution with evolution of nitrogen, yielding diphenylmethenylamidine (diphenyl-

formamidine). The formation of the latter substance is probably preceded by the hydrolysis of the azo-compound, thus:

$$NPh:N\cdot CH:NPh + H_2O = C_6H_6 + N_2 + NHPh\cdot CHO;$$

the formanilide then undergoes partial hydrolysis to aniline, which condenses with unchanged anilide to form diphenylformamidine.

When heated with benzaldehyde on the water-bath, the hydrazidine yields benzaldehydephenylhydrazone, α-formylphenylhydrazine, and an oil, which contains a small amount of a difficultly fusible substance, and is hydrolysed by dilute sulphuric acid to benzaldehyde, formic acid, and aniline. From these results the authors draw the conclusion that the interaction of the hydrazidine and benzaldehyde takes place in two directions, one resulting in the formation of formanilide and benzaldehydephenylhydrazone, the other giving rise to α-formyl-β-phenylhydrazine and benzylideneaniline, as shown in the following scheme:

$$\left.\begin{matrix} NHPh\cdot N:CH\cdot NHPh + \\ C_6H_5\cdot CHO \end{matrix}\right\} \begin{matrix} \nearrow\ NHPh\cdot N:CHPh + NHPh\cdot CHO \\ \searrow\ NHPh\cdot NH\cdot CHO + CHPh:NPh \end{matrix}$$

F. B.

Hæmatoporphyrin. IV. William Küster and Hugo Bauer (*Zeitsch. physiol. Chem.*, 1915, **94**, 172—190).—According to Willstätter (A., 1913, i, 1251) the basic properties of hæmatoporphyrin only appear after two ·CH:CH· bridges between carbon and nitrogen in two of the pyrrole nuclei of hæmin have been broken down, thus loosening the iron atom, which change is accompanied by a reduction of the resultant side-chains and an oxidation in another part of the molecule. Küster has already shown that such an intramolecular reduction and oxidation is unlikely (A., 1914, i, 95), and holds the opinion that the basic functions are already pre-formed, but dormant in hæmin.

During a new preparation of the dimethyl ether of hæmatoporphyrin, a small quantity of an iron compound which is most probably a methylated hæmin has been isolated. In addition, the authors have succeeded in removing iron from bromodimethylhæmin without producing more than a trace of hæmatoporphyrin. These facts strengthen the arguments against Willstätter's views.

Bromoacetylhæmin was shaken with a glacial acetic acid solution of hydrogen bromide, and the resulting solution was evaporated under reduced pressure, and the residue was dissolved in warm methyl alcohol. After a few hours, the clear solution was mixed with methyl-alcoholic potassium hydroxide, filtered from ferric oxide and potassium bromide, and then extracted with ether. The extract was washed until free from iron and then shaken with 10% hydrobromic acid (remaining brown, ethereal solution = *A*). The acid solution of tetramethylhæmatoporphyrin was left for four days, when the hydrolysis of the ester groups took place. Dimethoxyhæmatoporphyrin was finally isolated in crystals with no melting point. The replacement of hydrochloric acid by hydrobromic acid in the final hydrolysis (A., 1913, i, 1005) therefore gave a purer product than was previously obtained,

and the compound now agrees with Willstätter's description (*loc. cit.*). This dimethyl ether forms a *di-ammonium* salt and a *tri-silver* salt,

$$C_{36}H_{39}O_6N_4Ag_3.$$

It is readily converted into tetramethylhæmatoporphyrin by the action of diazomethane. In this respect, therefore, the hæmin derivative differs from bilirubin (this vol., i, 830).

The ethereal solution, *A*, contained the brown *compound*,

$$C_{38}H_{44}O_6N_4BrFe,$$

which is regarded as a dimethyl ester of dimethoxyhæmin, formed by the addition of hydrogen bromide to hæmin, followed by the replacement of bromine by methoxyl, and esterification. The substance was hydrolysed by methyl-alcoholic sodium hydroxide, and, on the addition of hydrochloric acid, esterification took place again and the analogous chlorine *compound* was precipitated.

On oxidising dimethoxyhæmatoporphyrin, the author, besides isolating hæmatic acid, obtained evidence of the formation of a *methoxylated imide*, $C_8H_{11}O_3N$, m. p. 59°. This may be methyl-ω-methoxyethylmaleimide, but should it be the isomeride, $NH<\begin{matrix}CO\cdot CMe\\ \|\\ CO\cdot C\cdot CHMe\cdot OMe'\end{matrix}$ then Willstätter's formula would be definitely disproved.

α-Bromodimethylhæmin loses most of its iron under the action of 25% hydrochloric acid at 150°, β-bromodimethylhæmin even more readily, without forming hæmatoporphyrin. The products crystallise in the same form as hæmin, but are insoluble in sodium hydroxide.

J. C. W.

Action of Peptolytic Enzymes on Polypeptides. Antonino Clementi (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 972—978).—The author has applied Sörensen's method of titration in presence of formaldehyde to the investigation of the action of peptolytic enzymes on polypeptides. In this way it is shown that *dl*-leucylglycine is not attacked by pancreatic juice, whereas exactly one-half of this racemic dipeptide is hydrolysed by an aqueous extract of dog's liver. This is the first quantitative experimental confirmation of the principle of the asymmetric action of the peptolytic enzymes of the organism on racemic polypeptides.

The formaldehyde titration method can be applied to far smaller amounts of polypeptides than Fischer's chemical method, is more rapid than Euler's electrometric method, and has the advantage over Abderhalden's polarimetric method that it is applicable to optically inactive polypeptides. Further, it yields rigorously quantitative results.

T. H. P.

The Amylase of Malt. P. Petit (*Compt rend.*, 1915, **161**, 39—40).—A diastase solution which will retain its activity constant for several weeks can be obtained in the following way: The malt is reduced to a fine powder and infused for twenty-four hours with aqueous acetone containing 30—35% of acetone by volume. The infusion is filtered and kept in the dark. The activity of this infusion drops very considerably during the first two days and then remains constant for twenty days. The action of light is injurious. If to the filtered

infusion an excess of a mixture of ether and acetone (1 : 2) is added and the clear liquid decanted after twenty-four hours, a residue is left, which when dried in a vacuum forms brown scales. An aqueous infusion of this residue shows very marked diastatic powers, and is markedly alkaline to methyl red. W. G.

Preparation of *o*-Hydroxyarylarsinic Acids. R. MEYER and K. OECHSLIN (Fr. Pat. 474056; from *J. Soc. Chem. Ind.*, 1915, **34**, 734).—The nitro-group in *o*-nitroarylarsinic acids is replaced by hydroxyl by the action of acids or alkalis, preferably in presence of reducing or oxidising agents or substances which destroy nitrous acid. For example, if one part of *p*-dimethylamino-*o*-nitrophenylarsinic acid is added to 0·5 part of carbamide in 10 parts of 60% sulphuric acid, carbon dioxide and nitrogen are evolved and *p*-dimethylamino-*o*-hydroxyphenylarsinic acid is precipitated on dilution with water and partial neutralisation. G. F. M.

Process for obtaining Mono- and Di-para-monoalkylaminophenylarsinic Acids. POULENC FRÈRES and K. OECHSLIN (Fr. Pat. 473704; from *J. Soc. Chem. Ind.*, 1915, **34**, 734).—*Mono-* and *di-p-monoalkylaminophenylarsinic acids* of the type $AsO(OH)_2 \cdot C_6H_4 \cdot NHR$ and $AsO(OH)(C_6H_4 \cdot NHR)_2$, where R may be an alkyl group or $\cdot CH_2 \cdot COOR$, are obtained by oxidising the product of the reaction between arsenic trichloride and the corresponding substituted amine in presence of pyridine. Thus amylaniline reacts with arsenic trichloride to produce *amylaminophenylarsinic acid* at 106—108°, and *diamylaminophenylarsinic acid* at 115—120°. Hydrogen peroxide is used as the oxidising agent, and the two acids are separated by precipitation with ether from absolute alcoholic solution, the secondary acid remaining in the mother liquors. *Methyl-* and *ethyl-aminophenylarsinic acids, phenylglycinearsinic acid*, and the corresponding diphenylated acids have also been prepared. G. F. M.

Method of Obtaining ortho- and meta-Nitroalkylphenylglycinearsinic Acids and their Reduction Products. POULENC FRÈRES and K. OECHSLIN (Fr. Pat. 473705; from *J. Soc. Chem. Ind.*, 1915, **34**, 734).—*o-* and *m*-Nitro-derivatives are produced by the nitration of alkylphenylglycinearsinic acids or their esters by a mixture of sulphuric acid and the theoretical quantity of nitric acid. The position taken up by the nitro-group depends on the concentration of the sulphuric acid. Thus, for example, the amyl ester of phenylmethylglycinearsinic acid can be converted into the 2-nitro-derivative by the action of diluted sulphuric and nitric acids at 42°. It is a deep yellow substance, m. p. 130°. The free acid obtained by saponification of the ester with sodium carbonate crystallises from water, and, on reduction with sodium hyposulphite, it is converted into

$$As_2[C_6H_3(NH_2) \cdot NMe \cdot CH_2 \cdot CO_2Na]_2.$$ G. F. M.

Aromatic Arsenic Compounds. X. ortho-Carboxylated Diaminodihydroxyarsenobenzene. P. KARRER (*Ber.*, 1915, **48**, 1058—1064. Compare this vol., i, 333).—A description of the

preparation of 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene-2 : 2′-dicarboxylic acid, a carboxylated derivative of salvarsan.

5-Nitro-2-aminobenzoic acid by the action of sodium arsenite on its diazotised solution was converted into *4-nitro-2-carboxyphenylarsinic acid*, $CO_2H\cdot C_6H_3(NO_2)\cdot AsO_3H_2$, colourless needles, which on reduction with sodium hyposulphite did not give the normal product, but was converted into a very soluble *compound*, probably a sulphamic acid; reduction by ferrous hydroxide, however, effected the formation of *4-amino-2-carboxyphenylarsinic acid*, $CO_2H\cdot C_6H_3(NH_2)\cdot AsO_3H_2$, the solution of which was immediately diazotised without isolation of the base, when on warming *4-hydroxy-2-carboxyphenylarsinic acid*,

$$CO_2H\cdot C_6H_3(OH)\cdot AsO_3H_2,$$

was obtained. This substance also was very easily soluble in water, and the resulting solution was therefore immediately warmed with hypophosphorous acid, which caused the separation of yellow flocks of *4 : 4′-dihydroxyarsenobenzene-2 : 2′-carboxylic acid*,

$$As_2[C_6H_3(OH)\cdot CO_2H]_2.$$

Oxidation by hydrogen peroxide reconverted this substance into 4-hydroxy-2-carboxyphenylarsinic acid, which was thus obtained in the form of colourless needles, whilst nitration with a mixture of sulphuric and nitric acids produced *5-nitro-4-hydroxy-2-carboxyphenylarsinic acid*, $CO_2H\cdot C_6H_2(NO_2)(OH)\cdot AsO_3H_2$, colourless needles, decomp. at 350—355°. The position assumed by the nitro-group in this new compound was demonstrated by reduction with a mixture of hypophosphorous and hydriodic acids in the presence of acetic acid with production of the corresponding yellow aminoarseno-derivative, namely, *5 : 5′-diamino-4 : 4′-dihydroxyarsenobenzene-2 : 2′-dicarboxylic acid*,

$$As_2[C_6H_2(OH)(CO_2H)\cdot NH_2]_2$$

(dimethylaminobenzaldehyde *derivative*, red), from which the arsenic atoms can be removed by heating with water and sodium acetate for ten hours at 100°, with formation of the 4-amino-3-hydroxybenzoic acid already known. D. F. T.

Physiological Chemistry.

Tributyrinase of Serum. G. A. Pietri (*Chem. Zentr.*, 1915, i, 1213; from *Arch. Farm. sperim.*, 1915, **19**, 63—80).—According to stalagmometric measurements, the activity of lipase contained in the blood towards tributyrin is not affected by very small amounts of sodium glycine, is restricted by small quantities, and slightly increased by larger amounts. Sodium chloride and bromide and potassium iodide cause restriction when above a certain concentration, but smaller amounts do not cause activation. With sodium fluoride, 0·1% causes restriction to the extent of 82%; 0·01%, 75%; 0·001%, 35%. Calcium chloride and magnesium sulphate restrict in relatively large quantities. Sodium butyrate restricts, whilst

glycerol is without noticeable action. Repeated blood-letting causes an increased power of ester fission in certain cases, but in others the power is decreased. H. W.

Value of Compounds of Amino-acids with Formaldehyde for the Nitrogenous Nutrition of Animals. Azzo Azzi (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 1125—1129).—Galeotti (A., 1913, i, 957) has shown that many properties of the amino-acids undergo profound change when these acids are treated with formaldehyde. The author finds that the compounds thus obtained, in conjunction with starch, etc., serve for a time for the nutrition of animals, which, however, gradually lose weight and die. T. H. P.

Metabolism of Amino-acids in the Organism. VII. Action of Hepatic Tissue on Amino-acids Added to Circulating Blood. Ugo Lombroso and Camillo Artom (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 1166–1172. Compare this vol., i, 616).—When blood containing dissolved amino-acids is circulated through the isolated liver of a dog, a marked diminution occurs in the amount of amino-acid, excepting in the case when leucine is employed. This diminution is not counterbalanced by increase in the content of amino-acid in the organ, this often remaining virtually unchanged. If blood alone is circulated, the proportion of amino-acids it contains exhibits an increase of more than 100%. In either case, the amount of ammonia in the liver always, and that in the blood sometimes, increases, but the magnitudes of these increases are not great enough to correspond with the quantity of amino-acid which disappears, excepting in the case of asparagine, with which a marked rise occurs in the amount of ammonia in the blood. In almost all cases the proportion of acetonic substances in the blood increases and that in the hepatic tissue diminishes; with leucine this change is especially pronounced, increases in both the blood and the liver being observed. T. H. P.

Separation of the Active Constituents of Hypophysis [Pituitary Gland]. F. Hoffmann, La Roche & Co. (D.R.-P. 282002; from *J. Soc. Chem. Ind.*, 1915, **34**, 686).—An alcoholic solution of hydrogen chloride is added to the chloroform extract of the powder obtained by triturating the extract of the pituitary gland, or the glands themselves, with sodium carbonate, and the solution is evaporated to dryness. On evaporating the aqueous extract, a small amount of crystalline residue is obtained which has the pharmacological action on the intestines ascribed to extracts of the pituitary gland. The portion of the extract which affects the blood pressure and exerts the peculiar action on the uterus is insoluble in chloroform, but is obtained on evaporating the neutralised alcoholic extract to dryness. G. F. M.

Oxidising Power of Animal Organs on Diphenols. Leopoldo López Pérez (*Anal. Fis. Quim.*, 1915, **13**, 299—304).—An investigation of the oxidising effect produced on diphenols by various

human organs, the excess of diphenol being estimated by liberating iodine from a solution of potassium iodide acidified with hydrochloric acid. A. J. W.

Origin of Cholesterol. S. Dezani and F. Cattoretti (*Chem. Zentr.*, 1915, i, 1214; from *Arch. Farm. sperim*, 1915, **19**, 1—9).—In extension of the investigations of Dezani (*Chem. Zentr.*, 1913, ii, 1765), it has been shown that mice, nourished with a cholesterol-free diet, can form cholesterol. Determinations of the latter by Windaus' method gave, in the case of animals deprived of cholesterol, an increase of from 0·175 to 0·252 gram of cholesterol, whilst normally fed animals only showed a slight increase. These increases point the more strongly to an endogenous formation of cholesterol, since the latter is separated in the fæces (about 0·076 gram). H. W.

Occurrence of an Abnormal Yellow Pigment in Urine. Ed. Justin-Mueller (*J. Pharm. Chim.*, 1915, [vii], **12**, 57—59).—Urine from a patient suffering from pleurisy and pneumonia exhibited a yellowish-red colour, which changed to golden-yellow when the urine was rendered alkaline. The yellow colour was not precipitated by basic lead acetate, and the yellow filtrate from the precipitate produced by this reagent showed an absorption band differing from that of urobilin. W. P. S.

Oxaluria. Ludwig Pincussohn (*Chem. Zentr.*, 1915, *i*, 1220; from *Deut. med. Woch.*, 1915, **41**, 132—134).— In a series of experiments which were undertaken with the object of investigating the action of light on animals into which certain dyes had been injected, it was found that decrease in allantoin was accompanied by an increase in the oxalic acid values. In dogs fed with purines, a slight increase in the separation of oxalic acid was detected, which also occurred without use of purines in an animal treated with eosin and then subjected to intense light; when purines were simultaneously given, the amount of oxalic acid was increased by five or six times. The ability of certain degradation products of purine to produce oxalic acid in the sensitised and illuminated animal body was also investigated. Xanthine caused an increase, whilst guanine and uric acid (per os) had no effect; uric acid given intravenously behaved similarly to purine. Experiments with nucleic acid did not lead to a definite result. H. W.

Comparison of Different Adrenalines and their Homologues According to their Action on the Arterial Pressure of a Dog Under Atropine. Marc Tiffeneau (*Compt. rend.*, 1915, **161**, 36—39. Compare Cushny, A., 1908, ii, 720; 1909, ii, 420; Barger and Dale, 1910, ii, 984).—The author suggests that, in order to compare different adrenalines, injections should be made into a chloralosed dog under the influence of atropine, and traces of the arterial pressure taken. The results show that by this method constant effects are produced by the same dose of an adrenaline

at different periods of the same experiment, even up to ten injections of different doses of this adrenaline or different adrenalines. The effects produced vary proportionately as the doses are increased or decreased, and this relative variation is constant. These facts hold good, of course, only for one and the same animal in a single experiment, and it is necessary from time to time to inject a standard dose, as, after a certain lapse of time, the animal reacts less regularly. The results obtained with different adrenalines show that *l*-adrenaline, whether natural or synthetic, is fifteen to twenty times more active than *d*-adrenaline. W. G.

Investigation of the Decomposition of Choline. G. Satta (*Chem. Zentr.*, 1914, ii, 723; from *Arch. Farm. sperim.*, **17**, 337—349). —Since, after the administration of choline, no choline and no increase of *N*-methyl (from muscarine, trimethylamine, etc.) is found in the urine, the author supposes that it is demethylated in the organism to methylhydroxyethylamine. This compound could further decompose into ethylene glycol and methylamine, or into methyl alcohol and aminoethyl alcohol. The production of glycol, according to the first alternative, would necessitate an increase in the oxalic acid excretion; but such an increase was never observed in the case of dogs which had been fed with lecithin, and a decomposition of the methylhydroxyethylamine in this sense cannot therefore be assumed. G. F. M.

Formation of Hippuric Acid from the Compound of Glycine with Formaldehyde. Gaetano Cicconardi (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 1130—1133. Compare Azzi, this vol., i, 857).—With dogs deprived of nitrogenous food, administration of benzoic acid causes an appreciable increase in the elimination of hippuric acid, but this increase becomes greater if glycine, and still greater if the compound of glycine with formaldehyde, is administered together with the benzoic acid. This compound can, therefore, be utilised by the organism for the synthesis of hippuric acid. T. H. P.

Chemistry of Vegetable Physiology and Agriculture.

Absorbtion of Cations and Anions by the Soil. A. DE DOMINICIS (*Chem. Zentr*, 1915, i, 391—392; from *Staz. sperim. agrar. Ital.*, 1914, **47**, 449—473).—Cations and anions are without exception absorbed by the soil. In certain experiments, negative absorption of Cl' and NO_3' was observed, but other experiments showed them to be absorbed in the same or greater measure than cations. The absorption of anions leads to the formation of insoluble substances, and, actually, anions are absorbed by electropositively, cations by

electronegatively, charged amorphous constituents of the soil. The extent of absorption is directly connected with the valency of the ions, increasing with increasing value of the latter. The relationship of the absorption of anion and cation to one another is the same for all soils; the total absorption, however, shows variations, and depends on the nature of the colloids and liquids of the soil.

H. W.

Mineral-acid Soils. Oscar Loew (*Chem. Zentr.*, 1914, ii, 428; from *Landw. Jahrb.*, **46**, 161—164).—The examination of Porto Rico acid, clay and loam soils showed that they contained only small amounts of humus and were poor in lime, the amount of lime being less than that of the magnesia. Protozoa were only found to a slight depth, whilst denitrifying organisms and *Azotobacter* occur only in small numbers. *Bacillus butyricus* was found in greater numbers, and *Rizobium leguminosarum* was widely distributed.

The acidity is estimated by treating 50 grams of the finely divided, air-dried soil with 200 c.c. of neutral 1% sodium acetate. In 100 c.c. of the filtrate the liberated acetic acid is titrated with $N/10$-sodium hydroxide.

It is suggested that the clay has the constitution represented by the formula $O[Si(OH)<^{O}_{O}>Al{\cdot}OH]_2$. N. H. J. M.

Action of Free Sulphur on Vegetation. G. Bosinelli (*Chem. Zentr.*, 1915, i, 1137; from *Staz. sperim. agrar. Ital.*, **48**, 175—184).—Experiments show that manuring with free sulphur accelerates the conversion of organic nitrogen compounds into ammonia. The action is, however, so slow that it is doubtful whether it is of any economic advantage. G. F. M.

Influence of Weather Conditions on the Amounts of Nitric Acid and of Nitrous Acid in the Rainfall near Melbourne, Australia. V. G. Anderson (*Report Brit. Assoc.*, 1914, 338—339).—The results of analyses of rain-water collected at Canterbury, near Melbourne, under different conditions of weather, showed that the amounts of nitrates and nitrites in the rain are very much greater with tropical than with antarctic types. With antarctic types of weather the amounts of nitrogen were from 0·002 (rear) to 0·005 kilo. per hectare (front). Of tropical rains, the spring and autumn type gave 0·018 kilo., the summer type 0·027 kilo., and the heat-wave type 0·039 kilo. per hectare. Intermediate results were obtained in antarctic depressions, with more or less tropical influence, and in tropical depressions with antarctic influence.

N. H. J. M.

Organic Chemistry.

Vapour Pressure of Ethane and Ethylene at Temperatures Below their Normal Boiling Points. G. A. Burrell and I. W. Robertson (*J. Amer. Chem. Soc.*, 1915, **37**, 1893—1902).—The saturated vapour pressures of ethylene and ethane have been determined from 1 to 760 mm. Data for other constituents of natural gas will appear in the future.

The apparatus is fully described and figured. The bath was a Dewar vessel filled with gasolene of low-boiling point, containing propane, butanes, pentanes, etc., which was cooled by forcing liquid air from a Dewar flask into a test-tube fixed in the bath.

The vapour pressures of ethane range from 1 mm. at −159·8° to 760 mm. at −89·3°, and of ethylene, from 4 mm. at −159·9° to 760 mm. at −103·9°. Straight line curves are obtained by plotting the common logarithm of the pressure against the reciprocal of the absolute temperature. The equations are, for ethane,

$$\log P = -831{\cdot}4/t + 7{\cdot}42,$$

and for ethylene, $\log P = -767{\cdot}8/t + 7{\cdot}433$. J. C. W.

Electrosyntheses in a Vacuum. S. M. Losanitsch (*Chem. Zentr.*, 1914, ii, 611—613; from *Bul. Soc. Ştiinţe Bucureşti*, 1914, **23**, 3—33).—Organic compounds under the influence of the silent electric discharge in a vacuum undergo in general either polymerisation or condensation. The reactions are very slow, and no means of accelerating them has been discovered. The author considers that the greenish-blue light of the discharge may possibly be the active agent in the reactions which would then be simply photosyntheses. The following are typical of the results obtained: *iso*Pentane was converted into *βη*-dimethyloctane, *decatylene* [*hexamethylcyclobutane*], $C_{10}H_{20}$, and a soft, yellowish-brown *compound*, $C_{45}H_{78}$. Unsaturated hydrocarbons polymerised rapidly, and ethylene gave a *compound*, $C_{14}H_{26}$, b. p. 100—110°/14 mm., a *compound*, $(C_{16}H_{26})_9$, m. p. 105°, and a *compound*, $(C_{16}H_{26})_n$, insoluble in organic solvents, m. p. 110°. Acetylene gave a brown solid *polymerisation product*, which exploded above 100°. Aromatic hydrocarbons also polymerised, benzene, for example, giving *dibenzene*, $C_6H_6{:}C_6H_6$, a viscous, colourless liquid, b. p. 135—137°/14 mm., from which crystals of diphenyl separated during distillation, *polymerised hydrobenzene*, $C_{72}H_{76}$, a yellow liquid, b. p. 110°, *soluble polymerised benzene*, $(C_6H_6)_{90}$, and *insoluble polymerised benzene*, $(C_6H_6)_n$. From toluene, xylene, cymene and mesitylene, a similar series of polymerised products was obtained, of which full particulars are given in the paper. The terpenes furnished polymerisation products consisting of mixtures of bimolecular liquids with solid multimolecular resinous substances. Thus pinene gave *dipinene*, $(C_{10}H_{16})_2$, b. p. 170—175°/14 mm., and *heptapinene*, a yellow resin, m. p. 100°. Similar products from limonene, camphene and menthene are also described. G. F. M.

The Polymerisation of Isoprene under the Influence of the Aluminium-Mercury Couple. J. Böeseken and J. Noorduijn (*Rec. trav. chim.*, 1915, **34**, 265—271).—Isoprene when heated on a water-bath in benzene solution with an aluminium-mercury couple for half-an-hour and the solution left for twenty-four hours yields a soluble and an insoluble product. The soluble product, when the benzene is distilled off, is left as an almost white resin, which when warm can be drawn out into threads, but on cooling sets to a hard, pulverulent mass, which is soluble in benzene, carbon disulphide, chloroform, toluene, etc. This substance is a polymeride of isoprene and has a very high molecular weight, since the boiling point of benzene is not raised by 0·001° on the addition of 5% of the substance. A determination of the iodine number shows it to be far more saturated than caoutchouc. Further, its viscosity is much lower than that of caoutchouc, and it cannot be vulcanised. The insoluble product is far less pure than the soluble, containing nearly 5% of ash. It possesses much the same properties as the soluble substance, being, however, more saturated, and consists probably of still more highly condensed poly-isoprenes.

W. G.

Apparent Specific Volumes of Alcohol in Aqueous Mixtures of Varying Concentration. Horace T. Brown (*Analyst*, 1915, **40**, 379—383).—The apparent specific volume, that is, the volume occupied by unit weight, of alcohol of all concentrations may be expressed by the formula: $1-(D-W)/W$, where D is the specific gravity of the mixture at 15·6°/15°, and W the weight of alcohol in grams in 1 c.c. In the case of alcoholic mixtures of low concentration (D 0 988 to 0·999) the apparent specific volume of the contained alcohol increases steadily with the dilution, and it follows from this that on progressive dilution within these limits the volume of the mixture must exceed the sum of the initial volumes of the constituents (water and alcohol), and that, under these conditions, there is an expansion of volume instead of a contraction. The critical point at which dilution ceases to produce contraction and begins to give rise to expansion occurs at a point corresponding very nearly with D 0·9652. This point would seem to mark the completed formation of a definite alcohol hydrate, during the formation of which continuous contraction takes place, and that the expansion which occurs on still further dilution is an expression of progressive dissociation of this hydrate. A hydrate having the composition $C_2H_5\cdot OH,8H_2O$ would contain 24·21% of alcohol; dilute alcohol having D 0·9652, at the critical point, contains 24·83% of alcohol by weight.

W. P. S.

The *iso*Oleic Acid from Seeds of Ivy. F. C. Palazzo and A. Tamburello (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 352—356).—The unsaturated acid constituting, in the form of glyceride, the greater part of the fatty substance of ivy seeds was formerly thought to be erucic acid (*Arch. Farm. Sci. affi.*, May, 1913), but is now shown to be an *iso*oleic acid identical with the petroselic acid found by Vongerichten and Köhler (A., 1909, i, 454) in parsley seeds. The fat constitutes 30—32% of the ripe, air-dried seeds, and has the following

characters: m. p. 25·2°, solidification point 21·4°, n^{40} 1·462, acid number (as oleic acid) 3·99, saponification number 190·5 (calculated for triolein, 190·4), iodine number 91·8 (calculated for triolein, 86·2). The petroselic acid, m. p. 29—30°, has the iodine number 89·85 and the acid number 200·1, and yields stearic acid quantitatively on reduction with hydrogen in presence of palladium black, and the dihydroxystearic acid, m. p. 122° (compare Vongerichten and Köhler, *loc. cit.*), on oxidation with permanganate. The melting point, 33—34°, given by Vongerichten and Köhler for petroselic acid differs from its solidification point by so much (6—7°) that it is probably inaccurate. T. H. P.

Isomerism of Erucic, Brassidic, and *iso*Erucic Acids. I. L. Mascarelli (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 583—585).—The various attempts to explain the isomerism of these acids are discussed. According to Bruni and Gorni (A., 1900, ii, 197, 714), in the case of *cis*- and *trans*-stereoisomerides containing an ethylene linking, the latter give solid solutions when dissolved in the corresponding saturated compounds, whereas the former do not; further, the *trans*-compounds have the higher melting points and the lower solubilities and are the more stable.

The cryoscopic method is, therefore, suggested as a means of investigating the isomerism of erucic, brassidic, and *iso*erucic acids (compare succeeding abstract). T. H. P.

Isomerism of Erucic, Brassidic, and *iso*Erucic Acids. II. L. Mascarelli and B. Toschi (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 586—590; *Gazzetta*, 1915, **45**, 313—319. Compare preceding abstract).—The authors have investigated cryoscopically these three acids in the corresponding saturated compound, behenic acid.

The cryoscopic constant of behenic acid is found experimentally to have the mean value, 44·4, whereas Raoult's empirical rule gives the number, 210·8. The latent heat of fusion of the acid is calculated by means of van't Hoff's formula to be 19·0 cals. per gram-mol.

In freezing behenic acid, erucic acid exhibits molecular weights slightly lower than the theoretical value; for this acid, therefore, the *cis*-configuration is probable. Brassidic and *iso*erucic acids give values respectively slightly and appreciably in excess of the calculated number, and are, consequently, probably *trans*-compounds. T. H. P.

β-Butyrolactone. Hjalmar Johansson (*Ber.*, 1915, **48**, 1262—1266).—Sodium β-bromobutyrate in aqueous solution undergoes a unimolecular change ($k = 0·009$ at 38°) with production of *β-butyrolactone*; the formation of the lactone is evident from the fact that the concentration of bromide ion increases much more rapidly than that of the hydrogen ion. By extracting the resulting aqueous solution with ether, the lactone was obtained as a mobile, highly refractive liquid, b. p. 72—73°/29 mm., which is not miscible with water in all proportions, and resembles acetone in odour. The reaction of the lactone with sodium or barium hydroxide appears to

be of the second order and is probably analogous to the corresponding change with valerolactone (compare Holmberg, A., 1912, ii, 1048), but is approximately twice as rapid. D. F. T.

Reactions of Ethyl Sodiomalonate. II. C. Loring Jackson and F. C. Whitmore (*J. Amer. Chem. Soc.*, 1915, **37**, 1915—1934. Compare this vol., i, 647).—In the earlier paper, it was stated that the action of an organic haloid, RX, on ethyl sodiomalonate would be to give the additive compound, $CO_2Et{\cdot}CHX{\cdot}CR(ONa){\cdot}OEt$, which would decompose into RNa (or RH in the presence of acids) and the halogenomalonic ester, $CHX(CO_2Et)_2$, if the radicle R happened to be more negative than the halogen X. The present paper deals with cases which fulfil these conditions. Twenty-nine compounds of the type RX which suffer this replacement of the halogen by hydrogen (or sodium) are reviewed, and the only feature common to them is the preponderating negative character of the radicle. This is due to the presence in the radicles of a very large variety of factors, such as nitrophenyl, phenylacetylene, or carboxylic ester groups, oxy-compounds of sulphur, sulphur alone (in thiocyanates), phenyl-ketones, or imides of dibasic acids. As a rule, the halogen is bromine, iodine or cyanogen, the cases of chlorine compounds which react in this way being restricted largely to such substances as the sulphonyl chlorides.

Two objections to the theory are discussed. In the first place, it involves the rapid disruption of a carbon–carbon linking, but this is not a real difficulty in view of the decomposition of chloral and hexabromodiacetyl. A second objection that it does not explain the action of sodium alkyloxides is met by showing that the two cases are not comparable. A point in favour of the theory is that it explains many complicated reactions of ethyl sodiomalonate which are otherwise obscure.

Kohler and MacDonald (A., 1899, i, 907) investigated the action of *p*-toluenesulphonyl chloride on ethyl sodioacetate and ethyl sodiomalonate, and their results support the above theory. The action of benzenesulphonyl chloride on ethyl sodiomalonate has now been examined. Solutions in benzene and ether were left together, when a precipitate separated which was washed several times with ether and then crystallised from hot alcohol. The ethereal washings contained ethyl ethanetetracarboxylate, and the alcoholic solution deposited sodium phenylsulphinate on cooling, whilst the mother liquor yielded on evaporation a secondary product, *ethyl sodiobenzenesulphonylmalonate*, $SO_2Ph{\cdot}CNa(CO_2Et)_2$. The latter compound was also formed by mixing ethyl chloromalonate and sodium phenylsulphinate in methyl alcohol, filtering from sodium chloride, and adding alcoholic sodium hydroxide.

An experiment on the action of ethyl sodiomalonate on 2 : 4-dinitro-1-bromothiolbenzene is described. The expected 2 : 4-dinitro-1-thiolbenzene was isolated.

Benzoyl chloride and bromide react with ethyl sodiomalonate to give ethyl benzoylmalonate, but it was hoped that benzoyl iodide, because of the less negative halogen, would tend to react in the above manner and yield some benzaldehyde. The main product was, however, ethyl

benzoylmalonate, but benzaldehyde may have been formed, although the evidence is given with reserve. The preparation of dry hydrogen iodide and benzoyl iodide is described.

p-Nitrobenzoyl chloride reacted in the normal way, giving *ethyl* p-*nitrobenzoylmalonate*, $NO_2 \cdot C_6H_4 \cdot CO \cdot CH(CO_2Et)_2$, white needles, m. p. 93°.

Ethyl bromomethanetricarboxylate, b. p. 168—170°, prepared by the action of bromine on ethyl methanetricarboxylate, reacted with ethyl sodiomalonate to form ethyl ethanetetracarboxylate and ethyl methanetricarboxylate.

α-Bromo-ββ-diphenylpropiophenone, prepared by brominating the product of the action of magnesium phenyl bromide on phenyl styryl ketone, reacted with ethyl sodiomalonate to give ethyl ethanetetracarboxylate and ββ-diphenylpropiophenone,

$$CHPh_2 \cdot CH_2 \cdot COPh.$$

From the products of the reaction of ethyl bromomethylmalonate with ethyl sodiomalonate and of ethyl bromomalonate with ethyl sodiomethylmalonate, in the cold, was isolated ethyl ethanetetracarboxylate, whereas the ethylenetetracarboxylate is formed when the mixture is heated (compare Ruhemann, A., 1894, i, 14; Bischoff, A., 1896, i, 527).

The formation of ethyl ethanetetracarboxylate in the above reactions, instead of a halogenomalonic ester as predicted by the theory, requires explanation. The additive compound of the haloid with the sodiomalonate is only decomposed on acidification, and it would seem that this would destroy the excess of ethyl sodiomalonate and so prevent it from reacting in the necessary way with the halogenomalonic ester. The acidification was brought about as a rule by shaking the benzene solution of the product with an aqueous acid, and, therefore, it may be assumed that sufficient ethyl sodiomalonate does really escape decomposition.

p-Nitrobenzyl thiocyanate, very pale yellow, long needles or slender prisms, m. p. 85—86°, and 2 : 4-*dinitrobenzyl thiocyanate*,

$$C_6H_3(NO_2)_2 \cdot CH_2 \cdot SCN,$$

m. p. 86—87°, have been prepared by mixing the chlorides and potassium thiocyanate in acetone. They have an irritating action on the skin. J. C. W.

Crystals of Maleic Anhydride. O. Mügge (*Centr. Min.*, 1915, 481—482).—Optical determinations are given. The positive double refraction is very high ($\gamma - \alpha = 0{\cdot}1955$ Na). There is a plane of gliding parallel to (101) of the rhombic crystals. The crystals evaporate on exposure to the air, but whilst fractured surfaces soon become dull, the crystal-faces retain their brightness. L. J. S.

Desmotropy of Derivatives of Ethyl Succinylsuccinate. Hugo Kauffmann (*Ber.*, 1915, **48**, 1267—1272).—The yellow product obtained by Baeyer (A., 1886, 445) in the interaction of ammonia and ethyl succinylsuccinate was at first believed by him to be the iminoderivative, a view which was also held later by Bogert and Dox (A., 1905, i, 841); later he inclined to the view that this compound was

ethyl *p*-diamino-$\Delta^{1:4}$-*cyclo*hexadiene-1 : 4-dicarboxylate. Liebermann (A., 1914, i, 658) described two isomeric forms of this product, a coloured and a colourless, the existence of which he ascribed to desmotropy between the two above structures. Re-investigation of the supposed desmotropy now shows that the pure product of the interaction of ammonia or an amine with ethyl succinylsuccinate is colourless, but that atmospheric oxygen readily causes partial oxidation to ethyl diaminoterephthalate, to which the colour is due. There is no case of desmotropy, the effect of potassium hydroxide in apparently influencing the substance so that a colourless desmotropic form is obtained is due to the removal of the yellow impurity as feebly coloured hydrolytic products, whilst the influence of heat or exposure to sunlight in solution in organic solvents in causing an apparent change from a colourless desmotropic form to a yellow isomeride, is in reality dependent on the occurrence of oxidation. Not only the condensation product with ammonia, but also those with primary amines are colourless, and exhibit this marked tendency towards oxidation.

D. F. T.

Some β-Substitution Derivatives of Butyric Acid containing Sulphur. J. M. Lovén and Hjalmar Johansson (*Ber.*, 1915, **48**, 1254—1262).—Crotonic acid was converted almost quantitatively into β-chlorobutyric acid by mixing with cold saturated hydrogen chloride solution and heating in a sealed tube at 70—80° for two hours; the *ethyl* ester of the product had b. p. 65—65·5°/15 mm. By treatment with saturated aqueous hydrogen bromide solution in the cold, crotonic acid was converted into β-bromobutyric acid, b. p. 117·5—118·5°/13 mm. These halogen-substituted acids in the form of their sodium salts reacted slowly in the cold with a solution of potassium xanthate, addition of acid precipitating impure *β-xanthylbutyric acid*,

$$CO_2H\cdot CH_2\cdot CHMe\cdot S\cdot CS\cdot OEt;$$

this oily product was converted into its potassium salt, when on treatment with concentrated ammonia solution it yielded xanthamide and the potassium salt of *β-thiolbutyric acid*, $SH\cdot CHMe\cdot CH_2\cdot CO_2H$, which was submitted to atmospheric oxidation in the presence of ammonia and a little ferric hydroxide, the final product being *β-disulphidodibutyric acid*, $S_2(CHMe\cdot CH_2\cdot CO_2H)_2$. This was not homogeneous, but consisted of two *isomerides*, presumably of the meso- and racemic type; these could be separated by crystallisation of the barium salt of the mixed acids, the constituent acids forming leaflets, m. p. 117° (*potassium* salt with $1H_2O$, deliquescent needles; *barium* salt with $2H_2O$, tablets or truncated pyramids), and scales, m. p. 117—119° (*potassium* salt, deliquescent needles; *barium* salt, spherical aggregates); the distinct nature of these acids is demonstrated by each depressing the m. p. of the other. Attempts to resolve the former and less soluble acid into enantiomorphous constituents by means of phenylethylamine were fruitless.

β-Sulphidodibutyric acid, $S(CHMe\cdot CH_2\cdot CO_2H)_2$, obtained by the action of alcoholic potassium sulphide solution on ethyl β-chloro- or β-bromo-butyrate with subsequent hydrolysis of the resulting ester, also consisted of a mixture of two *isomerides*, which again were separable

by recrystallisation of the *barium* salts; the less soluble salt yielded an acid, prisms, m. p. 84—85°, whilst from the mother liquors was obtained an acid, needles, m. p. 62—64°, exceedingly soluble in water. Oxidation of the former acid with potassium permanganate produced the corresponding *γγ'-dicarboxydiisopropyl sulphone*,

$$SO_2(CHMe\cdot CH_2\cdot CO_2H)_2,$$

rhombic tablets, m. p. 169·5—171°; *barium* salt, vitreous; *potassium* salt, non-crystalline; *potassium hydrogen* salt, leaflets. D. F. T.

A Misleading Statement as to Formose. Oscar Loew (*J. pr. Chem.*, 1915, [ii], **92**, 133—136).—The author claims that to him, and not to Butlerow, belongs the credit of having accomplished the first sugar synthesis. Formose, first described by the author in 1885, although a mixture, has the composition of a true sugar, whilst Butlerow's methylenitan (1861) consists mainly of the decomposition products of formose. F. B.

Effect of Temperature Control on the Yield of Products in the Destructive Distillation of Hard Wood. R. C. Palmer (*J. Ind. Eng. Chem.*, 1915, **7**, 663—669).—Results of experimental distillations, using 32 kilo. charges of wood, showed that lowering the temperature of the reaction and decreasing the rate of the distillation at the critical stage (the point at which exothermic reaction takes place) increased the yield of methyl alcohol by 45%, and that of the calcium acetate by 40%, as compared with the yields obtained on a manufacturing scale. The method of temperature control also gave 30% more methyl alcohol and 15% more calcium acetate when applied to distillations of large quantities of wood. The best results were obtained by slow distillation during the critical stage rather than by lowering the temperature at which the reaction took place; this was accomplished by first removing the moisture from the wood as rapidly as possible and then anticipating the period when destructive distillation or the critical stage began. At this point, the temperature of the furnace was decreased. Acetic acid is apparently much more subject to variations in the original wood decomposition than is methyl alcohol, and the yield of the acid is effected by the many interactions proceeding in the complex vapours in a large retort. W. P. S.

Pasteur's Principle of the Relation between Molecular and Physical Asymmetry. II. F. M. Jaeger (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 49—75).—An account is given of the crystallographic measurements of the optically active and inactive luteotriethylenediaminecobaltic salts of the type $[Co\ en_3]X_3$, which serve as the basis for the conclusions drawn in the previous paper (this vol., ii, 399).

r-*Luteotriethylenediaminecobaltibromide*, $[Co\ en_3]Br_3,3H_2O$: pseudo-ditrigonal-scalenoedrical, but probably monoclinic [$a : c = 1 : 0{\cdot}6794$], D^{25} 1·845, almost perfectly isomorphous with the corresponding chloride.

d-*Luteotriethylenediaminecobaltibromide*, $[Co\ en_3]Br_3,2H_2O$: ditetragonal-bipyramidal [$a : c = 1 : 0{\cdot}8399$]; gives an *X*-ray (Laue) diagram

which is identical with that furnished by the corresponding *l*-salt. The corresponding *l*-salt gave the same axial ratio. D 1·972.

dd-*Luteotriethylenediaminecobaltichlorotartrate*, $[Co\ en_3]Cl(C_4H_4O_6)$: triclinic-pedial $[a : b : c = 0{\cdot}6211 : 1 : 0\ 6521]$. For the corresponding bromotartrate, which appears to be completely isomorphous

$$[a : b : c = 0{\cdot}6208 : 1 : 0{\cdot}6528].$$

r-*Luteotriethylenediaminecobaltinitrate*, $[Co\ en_3](NO_3)_3$: rhombic-pyramidal, $[a : b : c = 0{\cdot}8079 : 1 : 1{\cdot}1279]$, D 1·709. The corresponding *l*-salt is described as rhombic-bisphenoidic

$$[a : b : c = 0{\cdot}8647 : 1 : 0{\cdot}5983],$$

D 1·729. The *d*-salt corresponds very closely with the *l*-form, giving $[a : b : c = 0{\cdot}8652 : 1 : 0{\cdot}6009]$, D 1·725.

r-*Luteotriethylenediaminecobalti-iodide*, $[Co\ en_3]I_3,H_2O$: rhombic-bipyramidal $[a : b : c = 0{\cdot}8700 : 1 : 1{\cdot}7399]$, D 2·270. The *d*-salt is also rhombic-bipyramidal $[a : b : c = 0{\cdot}8276 : 1 : 0{\cdot}7386]$, D 2·289. The *l*-salt gave $[a : b : c = 0{\cdot}8256 : 1 : 0{\cdot}7395]$ and D 2·288.

r-*Luteotriethylenediaminecobaltithiocyanate*, $[Co\ en_3](CNS)_3$: rhombic-bipyramidal $[a : b : c = 0{\cdot}8405 : 1 : 0{\cdot}8130]$, D 1·511. The *d*- and *l*-salts belong to the same group. The *d*-salt gave

$$[a : b : c = 0{\cdot}8494 : 1 : 0{\cdot}8376],$$

D 1·502; the *l*-salt identical ratios and D 1·496.

r-*Luteotriethylenediaminecobaltiperchlorate*, $[Co\ en_3](ClO_4)_3$: rhombic-bipyramidal $[a : b : c = 0{\cdot}8569 : 1 : 2{\cdot}7751]$, D 1·878. The *d*- and *l*-salts are rhombic bisphenoidic. The *d*-salt gave

$$[a : b : c = 1{\cdot}0572 : 1 : 0{\cdot}6801]$$

and D 1·881, and the *l*-salt $[a : b : c = 1{\cdot}0580 : 1 : 0{\cdot}6806]$, D 1 888.

r-Triethylenediaminecobaltinitrite, $[Co\ en]_3(NO_2)_3$, forms orange-yellow to brown, hexagonal plates, which on account of the high solubility could not be obtained in crystals suitable for measurement.

H. M. D.

Neutral-Salt Compounds of the Amino-acids and Polypeptides. P. Pfeiffer and Fr. Wittka (*Ber.*, 1915, **48**, 1289—1310).—The authors review the list of "neutral-salt compounds" obtained from the amino-acids with salts of the metals of the alkalis and alkaline earths (Pfeiffer and von Modelski, A., 1912, i, 949; 1913, i, 709) and classify these substances as molecular compounds analogous to that of calcium chloride with alcohol.

Several new compounds are described, the general method of preparation being crystallisation of a mixture from aqueous solution. From glycine are derived the *compounds*: $CaCl_2,3NH_2{\cdot}CH_2{\cdot}CO_2H$, tablets; $CaCl_2,Cu(CO_2{\cdot}CH_2{\cdot}NH_2)_2,3H_2O$, deep blue tablets. Betaine yielded $BaBr_2,2CH_2\langle\begin{matrix}CO---\\NMe_3\end{matrix}\rangle O,6H_2O$, hygroscopic leaflets, and $CuCl_2,CH_2\langle\begin{matrix}CO---\\NMe_3\end{matrix}\rangle O,3H_2O$, yellowish-green needles, m. p. near 183°. Sarcosine gave rise to $CaCl_2,NHMe{\cdot}CH_2{\cdot}CO_2H,4H_2O$, needles; $CaCl_2,3NHMe{\cdot}CH_2{\cdot}CO_2H$, tablets; $SrCl_2,NHMe{\cdot}CH_2{\cdot}CO_2H,4H_2O$, needles; $BaCl_2,NHMe{\cdot}CH_2{\cdot}CO_2H,4H_2O$, needles;

$$BaBr_2,NHMe{\cdot}CH_2{\cdot}CO_2H,4H_2O,$$

needles; $MgCl_2,2NHMe{\cdot}CH_2{\cdot}CO_2H,2H_2O$,

leaflets; $NaI,NHMe\cdot CH_2\cdot CO_2H,H_2O$, deliquescent, rhombic plates; $KBr,4NHMe\cdot CH_2\cdot CO_2H,4H_2O$, deliquescent needles;

$KI,4NHMe\cdot CH_2\cdot CO_2H,4H_2O$,

needles; $RbBr,4NHMe\cdot CH_2\cdot CO_2H,4H_2O$, needles.

With antipyrine were obtained the *compounds*,

$CaCl_2,3C_{11}H_{12}ON_2,9H_2O$,

needles, and $2CaCl_2,3C_{11}H_{12}ON_2,12H_2O$, needles.

[With J. von Modelski.]—Diketopiperazine yielded the *compounds*, $CaCl_2,C_3H_6O_2N_2,2H_2O$, prisms; $2LiCl,C_3H_6O_2N_2,9\frac{1}{2}H_2O$, needles, and $2LiBr,C_3H_6O_2N_2,2\frac{1}{2}H_2O$, needles. D. F. T.

Preparation of Sarcosine. Louis Baumann (*J. Biol. Chem.*, 1915, **21**, 563—566).—Methylamine hydrochloride is dissolved in formaldehyde solution, and potassium cyanide added. After three hours the brown mixture is extracted with ether, the extract partly dried and filtered, and the ether distilled off. The residue is suspended in barium hydroxide solution, and the nitrile saponified. From the filtered solution to which a little ammonia is added, the barium is removed by carbon dioxide, and the filtrate evaporated to a syrup. This is extracted with the least amount of boiling alcohol, and placed in the refrigerator. After twenty-four hours, sarcosine crystallises out, and is washed with cold alcohol. The yield is 25% of the theoretical. W. D. H.

Anhydrides and Amines from α-Amino-acids. F. Graziani (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 822—827. Compare this vol., i, 781).—Experiments made by heating alanine with glycerol, diphenylmethane, or acenaphthene show that glycerol is not necessary for the formation of *cyclo*alanylalanine (compare Balbiano, A., 1914, i, 1126), although it results in greatly increased yields (60%). This is probably due to the fact that both alanine and the anhydride are more soluble in glycerol than in either of the two above hydrocarbons, so that a lower temperature may be employed. The use of diphenylmethane or acenaphthene necessitates a higher temperature, at which the decomposition of alanine proceeds preferably in the direction of the formation of ethylamine, $NH_2\cdot CHMe\cdot CO_2H \longrightarrow NH_2Et + CO_2$.

T. H. P.

The Action of Oxalyl Chloride on Some Amides. Th. Figee (*Rec. trav. chim.*, 1915, **34**, 289—325).—In continuation of the work of Bornwater (compare A., 1911, i, 616) the author has examined the behaviour of a number of amides towards oxalyl chloride.

Oxalyl chloride reacts with propionamide in dry benzene to give *oxalyldipropionamide*, $COPr\cdot NH\cdot CO\cdot CO\cdot NH\cdot COPr$, micaceous scales, m. p. 216° (decomp.), together with some propionitrile and a small quantity of a *compound*, m. p. 104—106°.

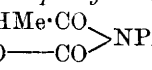
Phenylacetamide with oxalyl chloride gives *carbonyldiphenylacetamide*, $CO(NH\cdot CO\cdot CH_2Ph)_2$, lustrous plates, m. p. 114—116°.

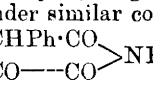
Acetanilide similarly gives *oxalyldiacetanilide*,

$NPhAc\cdot CO\cdot CO\cdot NPhAc$,

needles, m. p. 208—209° (decomp.). On hydrolysis, it yields oxalic acid.

Propionanilide reacts, best in equimolecular proportion, with oxalyl chloride to give 2 : 4 : 5-*triketo*-1-*phenyl*-3-*methylpyrrolidine*,



m. p. 138°. On hydrolysis, it gives with difficulty some oxalic acid. Phenylacetamide under similar conditions gives 2 : 4 : 5-*triketo*-1 : 3-*diphenylpyrrolidine*,  , yellow prisms, m. p. 238—239°, which on hydrolysis yields oxalic acid. On solution in sulphuric acid and shaking with benzene containing thiophen, it gave no blue colour, thus proving it not to be an isatin derivative.

Phenylurethane and oxalyl chloride in equimolecular proportions react in benzene solution, and, on allowing the benzene to evaporate spontaneously in the air, and recrystallising the residue from chloroform, N-*carbethoxyphenyloxamic acid*, $CO_2H\cdot CO\cdot NPh\cdot CO_2Et$, is obtained in needles, m. p. 140—141°.

Diphenylcarbamide and oxalyl chloride give diphenylparabanic acid, m. p. 206—207° [Biltz and Topp (A., 1913, i, 600) give m. p. 202°].

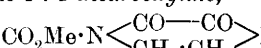
Oxalyl chloride (1 mol.) and methylaniline (4 mols.) in dry ether give dimethyloxanilide, needles, m. p. 111—111·5°. The substance, b. p. 249—251°, described under this name by Norton and Livermore, is in reality methylformanilide (compare A., 1887, 1038).

Phenylcarbamide and oxalyl chloride react in boiling ether to give, not only phenylparabanic acid as described by Biltz and Topp (*loc. cit.*), but also *oxalyldiphenylcarbamide*, $C_2O_2(NH\cdot CO\cdot NHPh)_2$, slender needles, m. p. 238—240°.

The author has prepared the two isomeric forms of methyl oxalyldi-α-phenylaminoacetate described by Meyeringh (A., 1913, i, 834), and subjected them to the action of liquid ammonia at 8—12° for two days. The isomeride, m. p. 169—170°, gave an *oxalyldi-α-phenylaminoacetamide*, m. p. 297°, and the isomeride gave an isomeric *amide*, m. p. 282°.

On heating ethyl phenylglycollate and oxalyl chloride together in boiling benzene solution, *oxalyldiphenylglycine ethyl* ester, crystallising with 1 mol. of benzene, $C_2O_2(NPh\cdot CH_2\cdot CO_2Et)_2 + C_6H_6$, was obtained, m. p. 104—105°. This compound was obtained free from benzene by distilling it with excess of water, and allowing the viscid oil formed to solidify, when it crystallised from chloroform in needles, m. p. 87—88°. Oxalic acid was liberated from this substance only on prolonged boiling with 10% aqueous potassium hydroxide. Gentle heating with this alkali for half-an-hour yielded *oxalyldiphenylglycine*, m. p. 217—219°. Attempts to prepare the corresponding amide by the action of liquid ammonia only yielded oxamide and phenylglycinamide.

Oxalyl chloride and methyl ethylenedicarbamate formed *methyl* 2 : 3-*diketopiperazine*-1 : 4-*dicarboxylate*,



m. p. 167°, which on hydrolysis gave oxalic acid. On treatment with liquid ammonia, it yielded oxamide and the *amide*,

$$NH_2\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot NH(CO_2Me)\cdot CO\cdot CO\cdot NH_2,$$

decomposing at 210—255°.

The interaction of diacetylethylenediamine and oxalyl chloride gave a *compound*, m. p. 204—205°, which was not characterised. W. G.

Some Derivatives of Mesoxalic Acid. D. J. VAN PROOYE (*Rec. trav. chim.*, 1915, [iii], **34**, 326—349).—The author has endeavoured to prepare from ethyl dihydroxymalonate and various amides a series of compounds comparable to the peptides, containing a mesoxalyl group, and similar in character to the derivatives obtained from oxalyl chloride by Bornwater (compare A., 1911, i, 616), but without success. On heating ethyl dihydroxymalonate and carbamide together in equimolecular proportions in absolute alcohol on a water-bath a compound is obtained, crystallising in slender needles, m. p. 132°, which is probably impure ethyl carbamidotartronate (compare Curtiss, Hill and Lewis, A., 1911, i, 366). On heating this with a second molecule of carbamide in alcohol, a *compound*, m. p. 98—100°, is obtained, which is probably the carbamide of ethyl carbamidotartronate, $NH_2\cdot CO\cdot NH\cdot CO\cdot C(OH)(NH\cdot CO\cdot NH_2)\cdot CO_2Et$. Attempts to condense ethyl dihydroxymalonate with various substituted carbamides and with glycine were unsuccessful, as were attempts to acetylate the dihydroxymalonic ester.

Ethyl diethoxymalonate was prepared by the method of Curtiss (A., 1897, i, 556), and from this a series of derivatives was obtained. On heating this ester with aqueous barium hydroxide on a water-bath the corresponding *barium* salt was obtained, which on trituration with water and addition to a warm silver nitrate solution yielded the *silver* salt, soluble in ammonia and reprecipitated by the addition of nitric acid as a fine white powder. The barium salt on treatment with the calculated quantity of sulphuric acid yielded *diethoxymalonic acid*, $C_7H_{12}O_6$, needles, m. p. 160°. All attempts to prepare the acid chloride were unsuccessful. The diethyl ester with aqueous or liquid ammonia gave *diethoxymalondiamide*, $C_7H_{14}O_4N_2$, m. p. 203—205°, and *ethyl diethoxymalonamate*, $C_9H_{17}O_5N$, m. p. 94—95°; the lower the temperature the higher the yield of monoamide. On heating the diamide with a large excess of acetyl chloride and a little acetic anhydride, or with acetic anhydride alone, *diethoxymalondiacetylamide*, $C_{11}H_{13}O_6N_2$, was obtained, m. p. 125—126°, which with liquid ammonia yielded, on keeping, the original diamide and acetamide. The monoamide could not be acetylated.

On heating diethoxymalondiamide and oxalyl chloride in dry benzene for six hours, *diethoxybarbituric acid*, m. p. 165°, was obtained, which was converted into alloxan by the action of nitric acid, and gave a *silver* salt, a white powder. This acid was also obtained by the condensation of ethyl diethoxymalonate and carbamide in absolute alcohol in the presence of sodium ethoxide.

Diethoxymalondimethylamide, $C_9H_{18}O_4N_2$, m. p. 170°, was obtained by the action of anhydrous methylamine on ethyl diethoxymalonate in a closed tube for two days at the ordinary temperature.

By the action of sodium urethane on ethyl diethoxymalonate in anhydrous ether and decomposition of the product with dilute sulphuric acid, *diethoxymalonyldiurethane*, $C(OEt)_2(CO\cdot NH\cdot CO_2Et)_2$, m. p. 114°, was prepared, which was decomposed by liquid ammonia, giving ethylurethane and diethoxymalondiamide.

A number of similar derivatives have been prepared in the same manner from ethyl diphenoxymalonate (compare Conrad and Brückner A., 1892, 39). Thus with liquid ammonia at the ordinary temperature, *ethyl diphenoxymalonamate*, $C_{17}H_{17}O_5N$, m. p. 196—197°, was obtained. With liquid ammonia in a sealed tube at 72° a mixture of the monoamide and *diphenoxymalondiamide*, $C_{15}H_{14}O_4N_2$, m. p. 269°, was obtained. This diamide, unlike the corresponding diethoxy-derivative, did not condense with oxalyl chloride.

On heating ethyl diphenoxymalonate and carbamide in absolute alcohol in the presence of sodium ethoxide in a sealed tube at 100° for four hours, *bis-(carboxyldiphenoxymalon)carbamide* [*carbonyldi-phenoxymalonamic acid*], $CO[NH\cdot CO\cdot C(OPh)_2\cdot CO_2H]_2$, m. p. 150—151°, was obtained. W. G.

Preparation of Acetylenic Nitriles and α-Haloid Derivatives of True Acetylenic Hydrocarbons. V. Grignard and Ch. Courtot (*Bull. Soc. chim.*, 1915, [iv], **17**, 228—231).—The authors have extended their method for the preparation of nitriles of the aliphatic, aromatic and cyclic series by means of the action of cyanogen chloride or cyanogen on magnesium derivatives of the hydrocarbons (compare A., 1911, i, 292) to the preparation of nitriles in the acetylene series. A good yield is obtained by this method, which has been applied to the preparation of amylpropiolonitrile [Δ^{α}-octinenonitrile], $CH_3\cdot[CH_2]_4\cdot C{:}C\cdot CN$, and phenylpropiolonitrile, $CPh{:}C\cdot CN$ (compare Moureu and Lazennec, A., 1906, i, 148). If in the latter preparation cyanogen chloride is replaced by cyanogen bromide, the main product of the reaction is β-bromo-α-phenylacetylene, CPh:CBr, b. p. 95—97°/11 mm. (compare Moureu and Delange, A., 1903, i, 312). Attempts to prepare the dicyano-derivative of acetylene by the action of cyanogen on the dimagnesium derivative of acetylene were not successful. W. G.

Hydrazides and Azoimides of Organic Acids. XXXII. Hydrazides and Azoimides of Succinic Acid. Theodor Curtius (*J. pr. Chem.*, 1915, [ii], **92**, 74—107. Compare A., 1895, i, 263; 1896, i, 34).—The first part of this paper deals with the preparation and reactions of the semihydrazide and semiazoimide of succinic acid, the second part with *N*-aminosuccinimide.

[With Ernst Muckermann.]—I. *Action of Hydrazine Hydrate on Ethyl Hydrogen Succinate, Succinamic Acid and Succinimide.* Contrary to the statement of Heintz (*Annalen*, 1859, **108**, 83), ethyl hydrogen succinate decomposes on distillation at ordinary pressure with the formation of succinic anhydride. The free ester reacts with hydrazine hydrate, yielding *hydrazine succinhydrazinate*,

$$NH_2\cdot NH\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H,N_2H_4,$$

slender needles or stout, hard crystals, m. p. 104°, whilst the barium

salt gives rise to succinylhydrazide, of which the *benzylidene* derivative, $C_2H_4(CO\cdot NH\cdot N{:}CHPh)_2$, has m. p. 223—224°.

Hydrazine succinamate, prepared from hydrazine hydrate and succinamic acid in alcoholic solution at the ordinary temperature, has m. p. 113°; in the absence of a solvent, the *ammonium* salt of succinhydrazinic acid, long, stout, transparent crystals, m. p. 122—123°, is produced.

The *benzylidene* derivative of succinhydrazinic acid,

$$CHPh{:}N\cdot NH\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H,$$

obtained together with benzaldazine by shaking an aqueous solution of hydrazine succinhydrazinate with benzaldehyde, forms slender needles or lustrous, soft, white leaflets, m. p. 164°; the *o-hydroxybenzylidene-*, m. p. 193°, *m-nitrobenzylidene-*, m. p. 207°, and *isopropylidene-*, m. p. 161° (from acetone) derivatives are also described; the *benzoyl* derivative forms microscopic, columnar crystals, m. p. 175.

The *semiazoimide* of succinic acid [*succinazoimic acid*],

$$N_3\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H,$$

prepared by the action of nitrous acid on the ammonium or hydrazine salt of succinhydrazinic acid, is a white, crystalline substance, which feebly explodes when heated, and reacts with alcohol in ethereal solution to form a pale yellow oil of aromatic odour, consisting probably of the *urethane*, $CO_2Et\cdot NH\cdot CH_2\cdot CH_2\cdot CO_2H$.

Attempts to convert the latter compound into β-aminopropionic acid by the action of alcoholic hydrogen chloride were unsuccessful; the product consisted of an inseparable mixture of ammonium chloride and a *substance*, crystallising in prisms, which reacts with benzenesulphonyl chloride to form a *substance*, m. p. 175°.

In addition to the semiazoimide of succinic acid, the interaction of ammonium and hydrazine succinhydrazinates with nitrous acid gives rise to *hydrazidisuccinic acid*, $N_2H_2(CO\cdot CH_2\cdot CH_2\cdot CO_2H)_2$. This forms lustrous, white leaflets, m. p. 212°, and is also produced by the addition of iodine to ammonium hydrazinate in alcoholic solution; the *ammonium* salt forms delicate radiating needles; the amorphous *silver* salt, $Ag_2A,\frac{1}{2}H_2O$, yields, with ethereal ethyl iodide, the *ethyl* ester, slender needles, m. p. 127—128°, which is converted by hydrazine hydrate in alcoholic solution into succinylhydrazide.

Succinamylhydrazide, $NH_2\cdot NH\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot NH_2$, prepared from succinimide and hydrazine hydrate in alcoholic solution at the ordinary temperature, crystallises in slender needles sintering at 138°, m. p. 145° with evolution of gas; *hydrochloride*, B,2HCl, m. p. 115—116° (decomp.); *benzylidene* derivative, m. p. 194°; *benzoyl* derivative, lustrous leaflets, m. p. 192° (decomp.).

Hydrazine ethyl sulphate, prepared from hydrazine sulphate and barium ethyl sulphate, forms long, colourless, very hydroscopic needles, m. p. 51°.

[With Karl Hochschwender and Hermann Thiemann.]—II N-*Aminosuccinimide*.—When heated with a small amount of hydrazine hydrate in alcoholic solution at 120—130°, ethyl succinate yields succinylhydrazide and N-*aminosuccinimide*, $\begin{matrix}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{matrix}\!\!>\!N\cdot NH_2$. The last-named substance is very hygroscopic and yields a *benzylidene*

derivative, m. p. 172—173°, *diacetyl* derivative, slender needles, m. p. 69—70°, and *hydrochloride*, decomp. 150°, which on treatment with sodium nitrite is converted into succinimide.

It reacts vigorously with hydrazine hydrate to form succinylhydrazide, and when heated or dissolved in strong aqueous sodium hydroxide gives rise to an amorphous *substance*, m. p. 258°, probably a cyclic hydrazide,

$$\begin{matrix}CH_2\cdot CO\cdot NH\\ |\\ CH_2\cdot CO\cdot NH\end{matrix} \text{ or } C_2H_4\begin{matrix}<CO\cdot NH\cdot NH\cdot CO>\\ <CO\cdot NH\cdot NH\cdot CO>\end{matrix}C_2H_4.$$

Attempts to prepare *N*-aminosuccinimide by the action of bromine and iodine on succinylhydrazide were unsuccessful. In aqueous solution, the former yields the preceding cyclic hydrazide, whilst the latter in alcoholic solution gives rise to hydrazine hydriodide and a *substance*, m. p. 233—234°, the *benzylidene* derivative of which sinters at 223°, m. p. 230°. F. B.

Some Higher Homologues of *cyclo*Hexane. O. M. Halse (*J. pr. Chem.*, 1915, [ii], **92**, 40—48).—The following homologues of *cyclo*hexane have been prepared by reducing the corresponding alkylbenzenes (A., 1914, i, 674) in glacial acetic acid solution by means of hydrogen in the presence of platinum black (Willstätter, A., 1912, i, 545). tert-*Butyl*cyclo*hexane*, $CMe_3\cdot C_6H_{11}$, b. p. 166—167°, D_4^{16} 0·8305, n_D^{16} 1·45562. *β*-cyclo*Hexyl-β-methylbutane*, $CMe_2Et\cdot C_6H_{11}$, b. p. 191—192°, D_4^{16} 0·8226, n_D^{16} 1·4538. *β*-cyclo*Hexyl-β-methylpentane*, $CMe_2Pr^{\alpha}\cdot C_6H_{11}$, b. p. 206—207°, D_4^{16} 0·8372, n_D^{16} 1·4670. γ-cyclo*Hexyl-γ-methylpentane*, $CMeEt_2\cdot C_6H_{11}$, b. p. 207—208°, D_4^{16} 0·8310, n_D^{16} 1·4574. γ-cyclo*Hexyl-γ-ethylpentane*, $CEt_3\cdot C_6H_{11}$, b. p. 222—223°, D_4^{16} 0·8388, n_D^{16} 1·4658. *β*-cyclo*Hexyl-βδ-dimethylpentane*,

$$CH_2Pr^{\beta}\cdot CMe_2\cdot C_6H_{11},$$

b. p. 220—221°, D_4^{16} 0·8304, n_D^{16} 1·4580. γ-cyclo*Hexyl-γ-methylhexane*, $CMeEtPr^{\alpha}\cdot C_6H_{11}$, b. p. 224—226°, D_4^{16} 0·8406, n_D^{16} 1·4646. *β*-cyclo*Hexyl-βε-dimethylhexane*, $CH_2Pr^{\beta}\cdot CH_2\cdot CMe_2\cdot C_6H_{11}$, b. p. 134—135°/30 mm., D_4^{19} 0·8512, n_D^{23} 1·4685. δ-cyclo*Hexyl-δ-methylheptane*,

$$CMePr^{\alpha}_2\cdot C_6H_{11},$$

b. p. 115—116°/13 mm., D_4^{19} 0·8483, n_D^{19} 1·4717. γ-cyclo*Hexyl-γ-ethylhexane*, $CEt_2Pr^{\alpha}\cdot C_6H_{11}$, b. p. 114—116°/13 mm., D_4^{19} 0·8547, n_D^{23} 1·4754. γ-cyclo*Hexyl-γζ-dimethylheptane*,

$$CH_2Pr^{\beta}\cdot CH_2\cdot CMeEt\cdot C_6H_{11},$$

b. p. 120—121°/10 mm., D_4^{19} 0·8717, n_D^{23} 1·4871. δ-cyclo*Hexyl-δ-ethylheptane*, $CEtPr^{\alpha}_2\cdot C_6H_{11}$, b. p. 129—130°/13 mm., D_4^{19} 0·8376, n_D^{23} 1·4598. δ-cyclo*Hexyl-βδζ-trimethylheptane*, $C_6H_{11}\cdot CMe(CH_2Pr^{\beta})_2$, b. p. 133—135°/11 mm., D_4^{19} 0·8396, n_D^{23} 1·4622. δ cyclo*Hexyl-δ-propylheptane*, $CPr^{\alpha}_3\cdot C_6H_{11}$, b. p. 133—135°/11 mm., D_4^{19} 0·8382, n_D^{23} 1·4606. δ-cyclo*Hexyl-β-methyl-δ-propylheptane*, $CH_2Pr^{\beta}\cdot CPr^{\alpha}_2\cdot C_6H_{11}$, b. p. 148—150°/10 mm., D_4^{19} 0·8441, n_D^{23} 1·4658. ε-cyclo*Hexyl-βεθ-trimethylnonane*, $C_6H_{11}\cdot CMe(CH_2\cdot CH_2Pr^{\beta})_2$, b. p. 156—158°/12 mm., $D_4^{20\cdot5}$ 0·8440, n_D^{20} 1·4666. ε-cyclo*Hexyl-βθ-dimethyl-ε-ethylnonane*, $C_6H_{11}\cdot CEt(CH_2\cdot CH_2Pr^{\beta})_2$, b. p. 162—164°/10 mm., $D_4^{20\cdot5}$ 0·8681, n_D^{20} 1·4789. ε-cyclo*Hexyl-βθ-dimethyl-ε-propylnonane*,

$$C_6H_{11}\cdot CPr^{\alpha}(CH_2\cdot CH_2Pr^{\beta})_2,$$

b. p. 190—192°/17 mm., $D_4^{20\cdot5}$ 0·8421, n_D^{20} 1·4646. ε-cyclo*Hexyl-βθ-*

dimethyl-ε-isobutylnonane, $CH_2Pr^{\beta}\cdot C(C_6H_{11})(CH_2\cdot CH_2Pr^{\beta})_2$, b. p. 162—163°/6 mm., $D_4^{20\cdot5}$ 0·8797, n_D^{20} 1·4905. F. B.

1 : 2 : 3-Trinitrobenzene, a New Trinitrotoluene [3 : 4 : 5] and Corresponding Dinitrohalogen Substitution Products. W. KÖRNER and A. CONTARDI (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 464—471).—1 : 2 : 3-*Trinitrobenzene*, $C_6H_3O_6N_3$, prepared by converting 2 : 6-dinitroaniline into the corresponding diazonium nitrate and treating the latter, in presence of ice, either with copper sulphate and sodium nitrite, or with the latter alone, forms large, faint green prisms, m. p. 127·5°.

3 : 4 : 5-*Trinitrotoluene*, $C_7H_5O_6N_3$, obtained similarly from 3 : 5-dinitro-*p*-toluidine, forms greenish-yellow, transparent prisms or plates, m. p. 137·5°, and, like the preceding compound, gives the original dinitroamine when treated with cold alcoholic ammonia. When oxidised with a mixture of chromic and concentrated sulphuric acids, it yields 3 : 4 : 5-*trinitrobenzoic acid*, $C_7H_3O_8N_3$, which forms white, opaque needles or yellowish-green, transparent, rhombic prisms ($+Et_2O$), m. p. 168° (decomp.), and, when boiled with water, is converted into 3 : 5-dinitro-4-hydroxybenzoic acid.

Treatment of the diazonium nitrate obtained from 2 : 6-dinitroaniline with cuprous or cupric chloride in presence of ice gives 1-chloro-2 : 6-dinitrobenzene.

1-*Bromo*-2 : 6-*dinitrobenzene*, $C_6H_3O_4N_2Br$, similarly obtained, forms shining, yellow prisms, m. p. 107°. 1-Iodo-2 : 6-dinitrobenzene may be prepared by the action of potassium iodide on the diazonium nitrate.

4-*Chloro*-3 : 5-*dinitrotoluene*, $C_7H_5O_4N_2Cl$, prepared from dinitrotoluene diazonium nitrate and cuprous or cupric chloride, forms stout, yellow, rhombic prisms, m. p. 114·5°.

4-*Bromo*-3 : 5-*dinitrotoluene*, $C_7H_5O_4N_2Br$, similarly obtained, forms yellow prisms, m. p. 118·4°.

4-*Iodo*-3 : 5-*dinitrotoluene*, $C_7H_5O_4N_2I$, prepared by the action of potassium iodide on the diazonium nitrate, forms lemon-yellow needles, m. p. 158°, and, like the two preceding compounds, yields the original 3 : 5-dinitro-*p*-toluidine when heated with alcoholic ammonia.

T. H. P.

Nitration of *p*-Bromotoluene. A. F. HOLLEMAN (*Rec. trav. chim.*, 1915, **34**, 283—288. Compare Wroblewski, A., 1875, 888; Hübner and Roos, A., 1874, 165).—An attempt to determine the relative amounts of 4 : 2- and 4 : 3-bromonitrotoluenes formed during the nitration of *p*-bromotoluene. The two isomerides were first prepared in the pure state and their properties determined. 4-Bromo-2-nitrotoluene has m. p. 45·5° and n_D^{50} 1·5750, and is only slightly decomposed by heating with an excess of sodium methoxide at 110° for twenty-four hours. 4-Bromo-3-nitrotoluene has m. p. 33°, n_D^{50} 1·5682, and on heating with sodium methoxide at 110° for twenty-four hours loses the whole of its bromine. *p*-Bromotoluene was nitrated by adding 10 grams of it in two equal portions to 20 c.c. of nitric acid (D 1·52) cooled on ice. The mixture was poured on to ice, extracted with benzene, the benzene distilled off, and the residue distilled in a

vacuum. The refractive index of the distillate was determined and the solidification point taken. These results gave the relative proportions of the two isomerides 1 : 2 : 4 and 1 : 3 : 4 as 56·3 : 43·7. Analysis by decomposition with sodium methoxide showed the mixture to contain 41·5% of the 1 : 3 : 4 isomeride. Calculations from theoretical considerations gave the relative proportions as

1 : 2 : 4/1 : 3 : 4 = 52·4 : 47·6. W. G.

The Nitration of Phenylethyl Chloride, $CH_2Ph\cdot CH_2Cl$. A. F. Holleman and (Mlle.) J. M. A. Hoeflake (*Rec. trav. chim.*, 1915, **34**, 261—264).—The authors have repeated von Braun's work on the nitration of phenylethyl chloride (compare A., 1913, i, 1318) and find that *p*-nitrophenylethyl chloride is not the only product, but that the oily product (*loc. cit.*) contains nearly 30% of the ortho-isomeride. This was shown by oxidising the total nitration product with alkaline permanganate, a mixture of *o*- and *p*-nitrobenzoic acids being obtained and separated. There was also indication of the formation of the meta-isomeride, but the amount was too small to allow of an exact proof. W. G.

Method of Preparation of Hydrocarbons having the Formula, $CHPh_2R$, R being an Aromatic Nucleus. F. Bodroux (*Compt. rend.*, 1915, **161**, 131—133).—Diphenylarylmethanes of the type $CHPh_2R$ can be readily prepared by the interaction of magnesium aryl bromides and diphenylbromomethane in ethereal solution. By this method excellent yields of triphenylmethane, diphenyl-*p*-tolylmethane, and diphenyl-α-naphthylmethane have been obtained. Attempts to replace the diphenylbromomethane by αα-dinaphthylchloromethane were not successful, as this substance with magnesium phenyl bromide in ethereal solution gave *s*-tetra-α-naphthylethane, and not the required phenyldinaphthylmethane. W. G.

2-Methylanthracene and Anthraquinone-2-carboxylic Acid. Otto Fischer and Kurt Reinkober (*J. pr. Chem.*, 1915, [ii], **92**, 49—54. Compare Fischer, A., 1875, 155, 1021; Weiler, A., 1875, 152).—An account of the behaviour of 2-methylanthracene towards halogens and also towards oxidising and reducing agents.

The action of chlorine at the ordinary temperature in dilute carbon disulphide solution yields a mixture (m. p. 191°) of penta- and hexa-chloro-2-methylanthracenes; prolonged action in more concentrated solution gives a mixture (m. p. 220°) of the nona- and deca-chloro-derivatives. In chloroform solution the product consists mainly of the hexachloro-derivative (m. p. 193°), whilst in benzene solution a mixture of the mono- and dichloro-derivatives is produced.

*meso*Dibromo-2-methylanthracene (Fischer, *loc. cit.*) is very stable towards reducing agents, is converted by solution in bromine into *pentabromo-2-methylanthracene*, pale yellow prisms, decomp. 300°, and yields, on oxidation with chromic acid in acetic acid solution, anthraquinone-2-carboxylic acid, of which the following salts are described: *ammonium*, white needles, which lose ammonia and pass into the free acid at 100—110°; *sodium*, white prisms containing

$1H_2O$; *barium*, $BaA_2,3H_2O$; *pyridine*, flat, white prisms; *quinoline*, needles.

2-Methylanthracene is not reduced by hydrogen iodide in boiling glacial acetic acid solution, but is converted by sodium and amyl alcohol into meso-2-*methyldihydroanthracene*, slender, white needles, m. p. 51°, which become brown on exposure to air and light. It is oxidised by chromium trioxide in glacial acetic acid solution and also by nitric acid (D 1·48) at 100° to 2-methylanthraquinone; at 170° nitric acid (D 1·5) gives rise to anthraquinone-2-carboxylic acid.

F. B.

Phototropy and Thermotropy. VII. Polymorphic Anisylidenearylamines Produced by Trituration and by the Influence of Actinic Light. Alfred Senier and Robert Benjamin Forster (T., 1915, **107**, 1168—1173. Compare T., 1915, **107**, 452).—The *p*-anisylidene derivatives of the usual primary aromatic amines have been prepared. No instances of phototropy or of triboluminescence have been observed; most of the compounds gave polymorphic forms by the prolonged influence of actinic light, and most of them were found to be thermotropic.

The following new compounds are described: *Anisylidene*-o-4-*xylidine*, colourless needles, m. p. 74—75° (corr.), the m-4-*xylidine*, pale yellow plates, m. p. 65—66° (corr.), and the p-*xylidine*, biscuit-coloured prisms, m. p. 68—69° (corr.); *anisylidene*-ψ *cumidine*, pale yellow prisms, m. p. 66° (corr.); *anisylidene*-o-*chloroaniline*, almost colourless needles, m. p. 61° (corr.), the m-*chloroaniline*, biscuit-coloured prisms, m. p. 54° (corr.), and the p-*chloroaniline*, colourless plates, m. p. 93—94° (corr.); *anisylidene*-m-*bromoaniline*, colourless needles, m. p. 61—62° (corr.), and the p-*bromoaniline*, very faint yellow needles, m. p. 120° (corr.); anisylidene-*p*-anisidine has m. p. 146—147° (corr.) (Hantzsch and Schwab gave 142°); *anisylidene*-o-*aminobenzoic acid*, yellow needles, m. p. 145° (corr.), the m-*aminobenzoic acid*, biscuit-coloured needles, m. p. 151—152° (corr.) (which is dimorphous), and the p-*aminobenzoic acid*, pale yellow needles, m. p. 196—197° (corr.); *dianisylidenebenzidine*, yellow plates, m. p. 257—258° (corr.).

C. S.

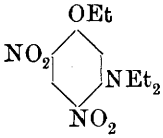
Derivatives of Phenyl Ether. Alfred N. Cook and Frank F. Sherwood (*J. Amer. Chem. Soc.*, 1915, **37**, 1835—1839. Compare A., 1901, i, 144; 1903, i, 163, 250, 337).—*o*-Nitrophenyl *p*-tolyl ether gave a *hexanitro*-derivative, $C_{13}H_6O_{12}N_6$, on boiling with concentrated nitric acid, and a *bromo*-derivative, $C_{13}H_{10}O_3NBr$, m. p. 23°, when left with diluted bromine and a trace of iodine. The latter was reduced to the *amino*-compound, which gave a *platinichloride*. The original substance also dissolved in sulphuric acid to form a *sulphonic acid*,

$$NO_2\cdot C_{13}H_{10}\cdot SO_3H,$$

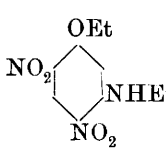
a solid, which was reduced to the *amino*-compound, and converted into the *chloride*, pale yellow plates, m. p. 69°. The *lead*, *barium*, *strontium*, *copper*, *cadmium* and *sodium* salts were, contrary to expectation, anhydrous.

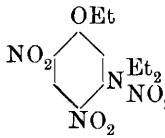
J. C. W.

Nitration of Diethyl-*m*-phenetidine. FRÉDÉRIC REVERDIN (*Bull. Soc. chim.*, 1915, [iv], **17**, 278—282; *Arch. Sci. phys. nat.*, 1915, [iv], **40**, 106—111. Compare this vol., i, 524).—*Diethyl-m-phenetidine*, a colourless oil, b. p. 286°, is obtained by the action of a slight excess of ethyl bromide on *m*-phenetidine. It has been nitrated under varying conditions with the following results.



To a solution of the base (3 grams) in glacial acetic acid (25 c.c.), cooled in ice and salt, 10 c.c. of nitric acid (D 1·52) were added, the temperature rising to 10°. The product was poured on to ice, and the precipitate, crystallised from benzene, yielded citron-yellow needles of 4 : 6-*dinitro*-3-*diethylamino*-1-*ethoxybenzene* (annexed formula), m. p. 94°. If the nitric acid was of D 1·4 and the mixture heated at 65—70°, then the product consisted of 4 : 6-*dinitro*-3-*ethylamino*-1-*ethoxybenzene* (annexed formula), citron-yellow, flat needles, m. p. 134°. A supposed *nitroso*-derivative, m. p. 75°, was isolated from the mother liquors in this nitration. It gave the Liebermann reaction, but the amount obtained was too small to permit of it being characterised. When diethyl-*m*-phenetidine or its dinitro-derivative, m. p. 94°, was nitrated in solution in acetic anhydride with nitric acid (D 1·52), the temperature being allowed to rise to 60—70°, the product was 4 : 6-*dinitro*-3-*ethylnitroamino*-1-*ethoxybenzene* (annexed formula), white needles, m. p. 112°. When this substance was heated with 10% alcoholic potassium hydroxide, 4 : 6-*dinitro*-3-*ethylamino*-1-*hydroxybenzene*, yellow, felted needles, m. p. 128—129°, was obtained, giving a *barium* salt, brown, slender needles. The yields in all these cases were much lower than in the nitration of dimethyl-*m*-phenetidine, and the products also had much lower melting points than the corresponding derivatives of dimethyl-*m*-phenetidine (*loc. cit.*). W. G.





Solubility of the Nitrophenols and Other Isomeric Disubstitution Products of Benzene. NEVIL VINCENT SIDGWICK, WILLIAM JAMES SPURRELL, and THOMAS ELLIS DAVIES (T., 1915, **107**, 1202—1213).—The solubility curves of certain isomeric disubstitution products of benzene have been determined with the hope of obtaining evidence of similarity, or otherwise, in constitution. In order to discover what is the normal influence of orientation on the solubility curves, the three cresols and the toluic acids, substances in which the possibility of any mutual reaction between the substituent groups is excluded, have been examined and their complete solubility curves in water determined by methods essentially the same as those used by Sidgwick, Pickford and Wilsdon (T., 1911, **99**, 1123). The critical solution temperatures are *o*-, *m*- and *p*-cresols, 162·8°, 147·0°, and 143·5° respectively; *o*-, *m*- and *p*-toluic acids, 161·2°, 162·2° and 159·1° respectively. The triple points are: *o*- and *p*-cresols, 8·0° and 8·7° respectively; *o*-, *m*- and *p*-toluic acids, 93·5°, 91·8°, and 142·0°

respectively. The results show that, in general, for any set of normal position-isomerides the liquid-liquid curves lie close together, the only considerable differences being in the points at which the solid-liquid curves branch off from them. It is noteworthy that the solubility curves of isomerides frequently cut one another; the measurement of the solubility at a few temperatures, therefore, may be very misleading.

Results quite similar to the preceding are obtained with *m*- and *p*-nitrophenols; the critical solution temperatures are 98·7° and 92·8° respectively, and the triple points, 41·5° and 39·6° respectively. The behaviour of *o*-nitrophenol is entirely different. Its solubility is never more than one-tenth of that of the other two isomerides; its critical solution temperature could not be measured, but is well above 200°; the triple point is at 43·5°. Without committing themselves to any definite view, the authors are of opinion, therefore, that there must be some difference in structure beyond the mere orientation between *o*-nitrophenol and its meta- and para-isomerides.

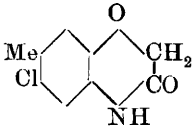
The solubilities of the three nitrophenols in toluene have been determined. The anomalous behaviour of the ortho-compound does not appear at all, and it is evident that the whole position of the curves is dominated by the m. p. of the pure compounds. C. S.

6-Chloro- and 6-Bromo-*m*-cresol. II. R. von Walther and K. Demmelmeyer (*J. pr. Chem.*, 1915, [ii], **92**, 107—132).—A continuation of previous work (this vol., i, 805).

6-Chloro-3-hydroxytoluene-4-sulphonic acid, prepared by the addition of 6-chloro-*m*-cresol to concentrated sulphuric acid at 70°, crystallises with $2H_2O$ in white leaflets, m. p. 93°, and is characterised by the ease with which it is reconverted, either by heating alone or with water or dilute hydrochloric acid, into the original chlorocresol. The following salts are described: *monosodium*, white, leafy crystals, solubility in water 1·82 grams per 100 c.c. at 14°; *disodium*, small needles; *potassium*, $KA,4H_2O$, and *barium*, leaflets; *calcium*, microscopic needles; *silver*, *ammonium* and *aniline*, prisms. It is converted by nitration into 6-chloro-2 : 4-dinitro-*m*-cresol. Attempts to prepare the chloride and esters by the usual methods were unsuccessful. 6-Chloro-*m*-cresol reacts with carbonyl chloride in alkaline solution, yielding *6-chloro-*m*-tolyl carbonate*, which crystallises in long, lustrous, silky, white threads, m. p. 141°, and when heated at 215° with sodium ethoxide is transformed into 6-chloro-3-hydroxy-*p*-toluic acid. With methyl and ethyl chloroformates it forms *6-chloro-*m*-tolyl methyl carbonate*, $C_6H_3MeCl\cdot O\cdot CO_2Me$, b. p. 135°/6 mm., and *6-chloro-*m*-tolyl ethyl carbonate*, b. p. 148°/8·5 mm., respectively.

*6-Chloro-*m*-tolyloxyacetic acid*, $C_6H_3MeCl\cdot O\cdot CH_2\cdot CO_2H$, prepared by the addition of hot, concentrated, aqueous sodium hydroxide to a molten mixture of chloroacetic acid and 6-chloro-*m*-cresol, forms white prisms, m. p. 176°; the *sodium*, *silver* and *lead* salts crystallise in white needles, the *ammonium* and *barium* salts in leaflets, the *potassium* salt in long, silky threads, the *calcium* salt in long prisms, and the *copper* salt in stellar aggregates of blue needles. It forms a *methyl* ester, m. p. 37°, *ethyl* ester, leaflets, m. p. 32°, and on nitration yields

6-*chloro*-4-*nitro*-m-*tolyloxyacetic acid*, which crystallises in clusters of long, pale yellow threads, m. p. 155°, and is reduced by sodium hyposulphite to 6-*chloro*-7-*methyl*-1 : 4-*benzoxazone*-4 (annexed formula), long, white needles, m. p. 187°.



6-*Chloro*-3-*hydroxy*-p-*tolualdehyde*, prepared by the addition of chloroform to a solution of 6-chloro-*m*-cresol in concentrated aqueous sodium hydroxide, forms long, pale yellow prisms, m. p. 68°; *sodium* salt, lustrous, golden-yellow leaflets.

6-*Bromo*-4-*nitro*-m-*cresol*, dark yellow needles, m. p. 124°, obtained by nitrating 6-bromo-*m*-cresol with the calculated amount of dilute acid in glacial acetic acid solution, is reduced by sodium hyposulphite to 6-*bromo*-4-*amino*-m-*cresol*, small, white leaflets, m. p. 116°, and yields the following salts: *ammonium*, light orange needles; *sodium*, red needles; *potassium*, dark red, prismatic needles; *calcium*, light orange leaflets; *barium*, dark orange leaflets; *silver*, dark red needles.

6-*Bromo*-2 : 4-*dinitro*-m-*cresol*, prepared in a similar manner, forms light yellow leaflets, m. p. 111°; the *sodium*, *potassium*, *ammonium*, *calcium*, and *silver* salts crystallise in orange needles or prisms; the *barium* salt in pale yellow needles.

6-*Bromo*-3-*hydroxytoluene*-4-*sulphonic acid*, obtained by the addition of 6-bromo-*m*-cresol to concentrated sulphuric acid at 70°, crystallises with $2H_2O$ in white leaflets, and on nitration is converted into 6-bromo-2 : 4-dinitro-*m*-cresol; the following salts are described: *ammonium*, *potassium*, *barium*, prisms; *sodium*, *calcium*, *silver*, leaflets; *aniline*, hexagonal prisms.

6-Bromo-*m* cresol reacts with carbonyl chloride and with methyl and ethyl chloroformates in aqueous sodium hydroxide solution to form 6-*bromo*-m-*tolyl carbonate*, white, prismatic leaflets, m. p. 130°; 6-*bromo*-m-*tolyl methyl carbonate*, colourless liquid, b. p. 158°/18 mm., and 6-*bromo*-m-*tolyl ethyl carbonate*, b. p. 167°/17 mm., respectively. With chloroacetic acid it yields 6-*bromo*-m-*tolyloxyacetic acid*, white, prismatic leaflets, m. p. 178°, of which the *sodium*, *potassium*, *ammonium*, *calcium*, *barium*, *silver*, *lead*, and *copper* salts are described; the *methyl* ester, m. p. 36°, and *ethyl* ester, m. p. 46°, crystallise in white leaflets. When heated with concentrated nitric acid and acetic anhydride it is converted into 6-*bromo*-4-*nitro*-m-*tolyloxyacetic acid*, $NO_2 \cdot C_6H_2MeBr \cdot O \cdot CH_2 \cdot CO_2H$, long, pale yellow needles or prisms, m. p. 177°.

6-*Bromo*-3-*hydroxy*-p-*tolualdehyde*, prepared from 6-bromo-*m*-cresol by the Tiemann-Reimer reaction, crystallises in pale yellow needles, m. p. 96°, the *sodium* salt in yellow leaflets. F. B.

Phenols. III. Preparation of Some New Substituted Cresols. Arthur J. Hill and Louis E. Graf (*J. Amer. Chem. Soc.*, 1915, **37**, 1839—1846).—In continuation of the work begun by Johnson and Hodge (A., 1913, i, 1055) some ethyl and propyl derivatives of *p*-cresol have now been prepared.

p-Tolyl methyl ether and acetyl chloride were condensed in light petroleum solution by means of aluminium chloride to 2-hydroxy-5-

methylacetophenone (Betteridge, *Diss.*, Breslau, 1898), and this was reduced by zinc amalgam and hydrochloric acid to 4-*methyl*-2-*ethylphenol*, $OH\cdot C_6H_3MeEt$, a pale yellow oil, b. p. 216—218°, which formed a *phenylurethane*, $NHPh\cdot CO_2\cdot C_6H_3MeEt$, square plates, m. p. 101°, when heated with phenylcarbimide and a trace of aluminium chloride.

p-Tolyl methyl ether was also condensed with propionyl chloride in light petroleum solution, in which medium demethylation proceeded simultaneously with condensation, the product being 2-hydroxy-5-methylpropiophenone (*ibid.*). This was reduced as above to 4-*methyl*-2-*propylphenol*, $C_{10}H_{14}O$, b. p. 128—130°/27 mm., the *phenylurethane*, $C_{17}H_{19}O_2N$, of which forms small needles, m. p. 99°. The same phenol was also prepared by a method which indicated the position of the propyl group. *p*-Cresol was converted into its allyl ether, and this was re-arranged into 4-methyl-2-allylphenol, the *phenylurethane*,

$$NHPh\cdot CO_2\cdot C_6H_3Me\cdot CH_2\cdot CH{:}CH_2,$$

of which has m. p. 68°. As the allyl derivative could not be reduced by any means, it was further rearranged into 4-methyl-2-propenyl phenol, $OH\cdot C_6H_3Me\cdot CH{:}CHMe$ (Claisen, A., 1913, i, 1175), and this gave the above 4-methyl-2-propylphenol on reduction with sodium and alcohol.

The value of zinc-amalgam as a reducing agent has been further tested in the case of some aminophenyl ketones. 3-Acetylamino-6-methyl-ω-chloroacetophenone, $NHAc\cdot C_6H_3Me\cdot CO\cdot CH_2Cl$, was boiled with zinc-amalgam and hydrochloric acid for several hours, and then the filtrate was rendered alkaline by ammonia and extracted. The unstable 4-*methyl*-3-*ethylaniline* (2-*ethyl*-p-*toluidine*) was converted into the *sulphate*, m. p. 178°. In the same way, 2-acetylamino-5-methyl-ω-chloroacetophenone was reduced to 4-methyl-3-ethylaniline, b. p. 217—220° (Willgerodt and Brandt, A., 1904, i, 657). J. C. W.

2-Aminophenyl Mercaptan. Th. Zincke and G. Siebert (*Ber.*, 1915, **48**, 1242—1254).—*o*-Aminophenyl mercaptan, obtained originally by Hofmann (A., 1880, 884; 1887, 823, 1039) from derivatives of benzothiazole, can also be conveniently prepared by reduction of 2 : 2′-dinitrodiphenyl disulphide in alcoholic solution with tin and hydrochloric acid. By reduction of 2-nitrophenyl methyl sulphide with zinc dust and water, there is obtained 2-aminophenyl methyl sulphide (compare Hofmann, *loc. cit.*), a strongly refractive oil, b. p. 133—134°/15 mm., with a faint odour resembling that of naphthalene; *hydrochloride*, long, silky needles; *formyl* compound, colourless prisms, m. p. 53—54°; *acetyl* derivative, leaflets, m. p. 102—103°; *benzoyl* derivative, needles, m. p. 96°. The base reacts with chloro-2 : 4-dinitrobenzene in alcoholic solution in the presence of potassium acetate, giving 2 : 4-*dinitro*-2′-*methylthioldiphenylamine*,

$$SMe\cdot C_6H_4\cdot NH\cdot C_6H_3(NO_2)_2,$$

deep red needles, m. p. 158—160°, which on reduction with alcoholic sodium sulphide undergoes conversion into 4-*nitro*-2-*amino*-2′-*methylthioldiphenylamine*, $SMe\cdot C_6H_4\cdot NH\cdot C_6H_3(NO_2)\cdot NH_2$, red crystals, m. p. 137°; this reacts with nitrous acid, yielding an *azimino*-derivative.

When the above aminophenyl methyl sulphide is diazotised and

treated with a solution of potassium cuprocyanide it is converted into *o-methylthiolbenzonitrile*, $SMe\cdot C_6H_4\cdot CN$, pale yellow needles, m. p. 40—41°, the hydrolysis of which with aqueous-alcoholic potassium hydroxide yields *o*-methylthiolbenzoic acid, $SMe\cdot C_6H_4\cdot CO_2H$, colourless needles, m. p. 169° (Friedländer, A., 1907, i, 335, gives m. p. 164°).

Oxidation of the acetyl derivative of aminophenyl methyl sulphide yields a sulphoxide derivative, the hydrolysis of which produces *o-aminophenyl methyl sulphoxide*, $NH_2\cdot C_6H_4\cdot SOMe$, a strongly refracting oil; *hydrochloride*, colourless needles, m. p. 167°; *acetyl* derivative, colourless crystals, m. p. 114—115°. Further oxidation of the acetylaminophenyl methyl sulphide with subsequent hydrolysis produces *o-aminophenylmethylsulphone*, $NH_2\cdot C_6H_4\cdot SO_2Me$, colourless leaflets, m. p. 65—66°; *acetyl* derivative, crystalline, m. p. 139—140°; *benzoyl* derivative, needles, m. p. 118—119°.

Treatment with chlorine in acetic acid solution converts the acetyl and benzoyl derivatives of aminophenyl methyl sulphide into chlorinated sulphoxide compounds; thus the benzoyl derivative gives *5-chloro-2-benzoylaminophenyl methyl sulphoxide*, $NHBz\cdot C_6H_3Cl\cdot SOMe$, silky needles, m. p. 138—139°, which is oxidisable by hydrogen peroxide in acetic acid solution to the corresponding *sulphone*, $NHBz\cdot C_6H_3Cl\cdot SO_2Me$, needles, m. p. 159—160°, and is hydrolysable to *5-chloro-2-aminophenyl methyl sulphoxide*, $NH_2\cdot C_6H_3Cl\cdot SOMe$, quadratic leaflets, m. p. 120—121°. Bromine does not exert any oxidising effect on the acetyl and benzoyl derivatives, the products in acetic acid solution being *3:5-dibromo-2-acetylaminophenyl methyl sulphide*, $NHAc\cdot C_6H_2Br_2\cdot SMe$, needles, m. p. 162—163°, and *3:5-dibromo-2-benzoylaminophenyl methyl sulphide*, crystals, m. p. 122—123°, respectively; in chloroform solution, on the other hand, unstable *perbromides* are obtained.

Phosphoryl chloride acts in characteristic manner on the acyl derivatives of aminophenyl methyl sulphide, converting the acetyl compound into 1-methylbenzothiazole, the benzoyl compound into 1-phenylbenzothiazole, the 3:5-dibromo-2-acetylamino-compound into *3:5-dibromomethylbenzothiazole*, $C_2H_2Br_2<\overset{N}{S}>CMe$, needles, m. p. 120—121°, and the 3:5-dibromo-2-benzoylamino-compound into *3:5-dibromo-1-phenylbenzothiazole*, needles, m. p. 168—169°. The acyl derivatives of *o*-aminophenylmethylsulphone also react with phosphoryl chloride, the acetyl and benzoyl derivatives yielding *1-methyl-2-benzosulphoneazole*, $C_6H_4<\overset{N}{SO_2}>CMe$, leaflets, m. p. 149—150°, and *1-phenyl-2-benzosulphoneazole*, $C_6H_4<\overset{N}{SO_2}>CPh$, a crystalline powder, m. p. 169—170° respectively; *2-benzosulphoneazole*, $C_6H_4<\overset{N}{SO_2}>CH$, leaflets, m. p. 105—107°, was obtained by the action of phosphoryl chloride on *o*-aminophenylmethylsulphone in the presence of formic acid. On the other hand, in the interaction of the acyl derivatives of 2-aminophenyl methyl sulphoxide and phosphoryl chloride, reduction of the former occurs, so that the product from the acetyl derivative is methylbenzothiazole.

o-Aminophenyl methyl sulphide when heated with methyl iodide and methyl alcohol for six hours at 100° is converted into *o-methylthiolphenyltrimethylammonium iodide*, $SMe\cdot C_6H_4\cdot NMe_3I$, prisms, m. p. 162—163° (decomp.), which forms two *additive* compounds with iodine, namely, $C_{10}H_{16}NSI_3$, monoclinic leaflets, and $C_{10}H_{16}NSI_5$, blue-black needles. The decomposition of the iodide which occurs at the m. p. gives rise to *o-dimethylaminophenyl methyl sulphide*, $NMe_2\cdot C_6H_4\cdot SMe$, a colourless oil, b. p. 130°/20 mm., *hydrochloride*, deliquescent needles.

D. F. T.

3-Thiolphenanthrene and Some of its Derivatives. Ellen Field (T., 1915, **107**, 1214—1217).—*3-Thiolphenanthrene*, $C_{14}H_{10}S$, rhombohedral plates, m. p. 112—113°, b. p. 205—210°/2 mm., prepared by reducing phenanthrene-3-sulphonyl chloride by dilute sulphuric acid and zinc dust, is very easily oxidised, best by an alcoholic solution of iodine, to *phenanthrene 3-disulphide*, $(C_{14}H_9S)_2$, stout needles, m. p. 165°, and forms a *methyl ether*, needles, m. p. 100°, b. p. 240°/12 mm., *acetyl* derivative, needles, m. p. 93°, and *benzoyl* derivative, needles, m. p. 115°, the first of which is oxidised by chromic acid to *3-phenanthraquinonylmethylsulphone*, $C_{14}H_7O_2\cdot SO_2\cdot CH_3$, orange needles, m. p. 280—282° (decomp.). When the yellow precipitate obtained by treating 3-thiolphenanthrene with cold alcoholic lead acetate is dried at 100° and distilled under diminished pressure, *diphenanthryl 3-sulphide*, $(C_{14}H_9)_2S$, cream-coloured needles, m. p. 225°, b. p. 360°/2 mm., is obtained.

C. S.

Sulphonation of Quinol. Joh. Pinnow (*Zeitsch. Elektrochem.*, 1915, **21**, 380—388).—The author has studied the kinetics of the sulphonation of quinol. It is shown that the sulphonation of quinol is a unimolecular reaction, if an excess of sulphuric acid with respect to the quinol and its monosulphonic acid is used, and if the concentration of sulphuric acid does not exceed 26*N*. Under these conditions the reaction is reversible. The hydrolysis of the monosulphonic acid is brought about by the sulphuric acid which exists as mono- and di-hydrate in the solution, and not by the ions or the undissociated acid. The introduction of a single sulphonic acid group depends on the monohydrate of sulphuric acid, and the introduction of the second sulphonic acid group at 100° is due to the anhydrous sulphuric acid. Since the water formed in the sulphonation retards the formation of the monosulphonic acid, prolonged heating causes the formation of by-products, and an excess of sulphuric acid yields the disulphonic acid; it is shown that the formation of the quinolmonosulphonic acid is best carried out by adding a slight excess of sulphuric acid to quinol and heating in an evacuated flask. The monosulphonate is only slightly and slowly hydrolysed at 100°.

J. F. S.

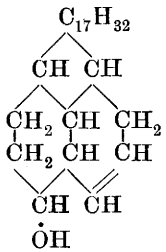
Oxidation Product of Pyrogallol. Maximilian Nierenstein (T., 1915, **107**, 1217—1220).—*2 : 3 : 2′ : 3′ : 2″ : 3″-Hexahydroxytriphenoquinone*, $O{:}C_6H_2(OH)_2{:}C_6H_2(OH)_2{:}C_6H_2(OH)_2{:}O$, yellow needles,

m. p. 274—275° (decomp.), prepared together with other products by oxidising with a r a solution of pyrogallol in 2*N*-potassium hydroxide, forms a *phenylhydrazone*, $C_{18}H_6(OH)_6(N{\cdot}NHPh)_2$, brown needles, m. p. about 304—308° (decomp.), and p-*bromophenylhydrazone*, $C_{30}H_{22}O_6N_4Br_2$, red needles, m. p. about 312—314° (decomp.), and is converted by reduction with zinc dust and hot acetic anhydride and subsequent hydrolysis into 2 : 3 : 2′ : 3′ : 4′ : 2″ : 3″ : 4″-*octahydroxy*-1 : 4-*diphenylbenzene*, $C_{18}H_6(OH)_8$. This substance crystallises from water in needles containing $1H_2O$, m. p. 329—333° (decomp.), whilst the anhydrous compound darkens at about 250—270° and appears to melt at 300—320°; it forms an *octa-acetyl* derivative, needles, m. p. 262—264°, and *octa*-p-*nitrobenzoyl* derivative, cubes, m. p. 250—252°, yields a substance, m. p. 209·5° (corr.), which is probably 1 : 4-diphenylbenzene, by distillation with zinc dust, and is oxidised in alkaline solution by various reagents to a red substance which resembles purpurogallin in every way. C. S.

Cholesterol. XXII. The Action of Perbenzoic Acid on Cholesterol. THEODOR WESTPHALEN (*Ber.*, 1915, **48**, 1064—1069). —It has been shown that organic peroxides such as perbenzoic acid can be applied to the oxidation of ethylenic compounds, the $-C{:}C-$ linking being converted into a $-C\overset{\diagup\diagdown}{-}C-$ (O) group (Prileschaev, A., 1910, i, 86, 295; 1911, i, 255, 604). When cholesterol is submitted to the action of this reagent in boiling chloroform solution, two isomeric oxides are produced. The less soluble *α-cholesterol oxide*, $C_{27}H_{46}O_2$, pearly tablets, m. p. 140—141°, in the Liebermann-Burchard test gives a red colour changing to violet, and forms a sparingly soluble additive *compound*, needles, decomp. above 230°, when mixed with digitonin in alcoholic solution; when heated with water at 115°, the oxide is converted into α-cholestantriol, $C_{27}H_{48}O_3$, needles, m. p. 238—239°, identical with the compound described by Pickard and Yates (T., 1908, **93**, 1680) as dehydrocholestantriol, $C_{27}H_{46}O_3$. α-Cholesterol oxide under the action of boiling acetic anhydride passes into an *acetyl* derivative, $C_{27}H_{45}O_2Ac$, needles, m. p. 98°, a solution of which in acetic acid containing a little sulphuric acid gradually deposits crystals, m. p. 166°, of *cholestantriol diacetate*, $C_{31}H_{52}O_5$; an attempt to acetylate the remaining hydroxyl group in this compound by using acetic anhydride containing a little sulphuric acid yielded the *diacetate* of a cholestendiol, $C_{31}H_{50}O_4$, leaflets, m. p. 125°, due to dehydration. Oxidation of α-cholesterol oxide acetate with chromic acid in acetic acid solution gave the same product as was obtained earlier by Pickard and Yates in the oxidation of the acetate of "dehydrocholestantriol," but in accordance with the authors' view of the composition of "dehydrocholestantriol," the product is now described as a cholestanendiol monoacetate, and to the derivatives of this substance, formulæ are attributed containing two more hydrogen atoms than were given in the earlier formulæ.

The above chemical changes are represented by formulæ based

on the structure (annexed) for cholesterol, the carbon atoms on each side of the double bond being the positions at which the majority of the changes occur, whilst in the cholestendiol derivative the double bond is supposed to have moved to the neighbouring position so as to be adjacent to the tertiary carbon atom common to the two hexatomic rings.



The isomeric β-cholesterol oxide, m. p. 100—110°, gives an *acetyl* derivative, needles, m. p. 114°, and an insoluble additive *compound* with digitonin. The investigation of the β-oxide was incomplete, and it is also not possible at present to say whether either of these oxides is present among the oxidation products obtained with potassium permanganate (Lifschütz, A., 1907, i, 315). D. F. T.

Esterification. VI. Esterification of Benzoic Acid by Mercaptans. L. S. Pratt and E. Emmet Reid (*J. Amer. Chem. Soc.*, 1915, **37**, 1934—1948. Compare A., 1910, i, 481).—A careful study of the esterification of acids by mercaptans and of the hydrolysis of thiol esters has been commenced in order to determine whether the limits of the reactions are comparable with those observed in the case of alcohols.

Methyl, ethyl, propyl, *iso*butyl, and *iso*amyl mercaptans were available, whilst the esters were prepared from potassium thiolbenzoate by the agency of methyl sulphate or the alkyl bromide. The methyl thiolbenzoate had b. p. 134°/25 mm., D_{25}^{25} 1·1381; the ethyl ester had b. p. 146°/31 mm., D_{25}^{25} 1·0977; and the propyl compound had b. p. 144°/13 mm., D_{25}^{25} 1·0724.

The benzoic acid and the mercaptan were weighed into tubes, and the esters were also weighed in tubes and mixed with a few drops of water, and then the sealed tubes were heated at various temperatures ranging from 193 to 243°, and for 67—240 hours in a special electric oven, which is described. After transfering the contents of a tube into a flask, the excess of mercaptan was removed by a current of pure air, and then the benzoic acid was titrated.

Concordant results were obtained in the esterification series, but not in the hydrolysis series, and this requires further investigation. The stability of the esters was found to decrease with increasing molecular weight. Methyl thiolbenzoate is stable at 243°, whilst the ethyl ester is slightly decomposed at that point, but not at 220°, and the propyl compound is unstable at the lower temperature. The limits of the reaction were slightly improved by rise of temperature, but they were very much lower than in the case of the alcohols, and decreased, rather than increased, with rise of molecular weight. For 243°, the limits observed were: methyl 19·6%, ethyl 15·4%, propyl 15·1%, *iso*butyl 12·7%, *iso*amyl 10·8%. J. C. W.

Aromatic Nitro-derivatives. II. Trinitrobenzoic Acids and Dinitrotoluidines Corresponding with β- and γ-Trinitrotoluenes. Michele Giua (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 484—489; *Gazzetta*, 1915, **45**, 345—352).—2 : 3 : 4- and 2 : 4 : 5-

Trinitrobenzoic acids, prepared by oxidation of the corresponding trinitrotoluenes by means of nitric acid or a mixture of chromic and concentrated sulphuric acids, are very readily esterified, and thus behave in accordance with V. Meyer's rule concerning the esterification of substituted benzoic acids. Will (A., 1914, i, 509) found that, when treated in acetone solution with ammonia, 2 : 3 : 4- and 2 : 4 : 5-trinitrotoluenes give respectively green and blue colorations. The author finds that these colorations gradually change to a more or less intense red, and that in this reaction one of the nitro-groups is replaced by an amino-group; this replacement is probably preceded by addition of a molecule of ammonia to the nitro-group, just as is the case with 2 : 4 : 6-trinitrotoluene (compare Korczyński, A., 1908, i, 977).

2 : 3 : 4-*Trinitrobenzoic acid*, $C_7H_3O_8N_3$, forms large prisms, m. p. 202—203°, and emits carbon dioxide at 219°; with alkali it gives a dark red coloration, this disappearing after the addition of 1 mol. of the alkali. Its *ethyl* ester, $C_9H_7O_8N_3$, forms needles, m. p. 79—80°, and its *silver* salt turns yellow in the air and explodes violently at above 230°.

2 : 4 : 5-*Trinitrobenzoic acid* forms shining laminæ melting and evolving carbon dioxide at 190—191°; with alkali it gives a reddish-yellow coloration. Its *ethyl*, m. p. 84°, and *methyl* esters, m. p. 102°, and its *silver* salt, which explodes when heated, were prepared.

The *dinitrotoluidine*, prepared from 2 : 3 : 4-trinitrotoluene, forms long, shining needles, m. p. 93—94°, and the *isomeride* obtained from the 2 : 4 : 5-compound, needles, m. p. 192—193°. T. H. P.

Basic Copper Salicylate. W. Œchsner de Coninck (*Bull. Soc. chim.*, 1915, [iv], **17**, 232—234. Compare this vol., i, 535, 536).—*Basic copper salicylate*, $C_6H_4<^{CO_2}_{O}>Cu,H_2O$, is readily obtained by stirring the hydrated normal salt in ethyl ether for half-an-hour, washing the product with ether, and leaving it to dry under a bell-jar. When heated in a current of dry nitrogen at 100°, it loses its water, and is converted into the anhydrous basic salt. A hemihydrate was isolated by heating for a shorter time. The monohydrate crystallises from warm water in slender, felted needles. When heated in the presence of moisture, this basic salt was decomposed, giving phenol, carbon dioxide and copper oxide. The salt was treated with various acids, bases and salts, and the products examined for the presence of salicylic acid. The results were positive with warm hydrochloric acid, strong or dilute, cold concentrated nitric acid, and warm acetic and propionic acids; negative with sulphuric acid, concentrated or dilute, aqua regia, hydrobromic acid and oxalic and tartaric acids in saturated aqueous solutions. The results were negative with all the bases tried. With potassium ferrocyanide in aqueous solution a precipitate of copper ferrocyanide appeared in a few minutes. W. G.

Basic Salicylates. W. Œchsner de Coninck and Gérard (*Bull. Soc. chim.*, 1915, [iv], **17**, 282—285).—For the most part a more detailed account of work already published (compare this vol., i, 536;

preceding abstract). Attempts to prepare basic magnesium and bismuth salicylates from their normal salts were not successful.

W. G.

Vanadylsalicylates. G. A. Barbieri (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 408—411).—The author has prepared various vanadylsalicylates, $VO(O{\cdot}C_6H_4{\cdot}CO_2M)_2$, which are white or pale yellow in the solid state and green in solution, whereas ordinary vanadyl salts are green or blue and vanadyltartrates (compare this vol., i, 380) violet. The silver salt could not be prepared, owing to the reducing action of the vanadyl residue on silver nitrate. The vanadylsalicylates, like the cupri- and pallado-salicylates, are moderately stable; they are crystallisable from water and are not decomposed by dilute alkali solutions. Addition of soluble salts of calcium, barium, thallium or ethylenediamine to aqueous solutions of alkali vanadylsalicylates precipitates the corresponding salts as white, crystalline powders. *m*- and *p*-Hydroxybenzoic acids form complex salts with neither copper, nor palladium nor vanadyl, the complex salicylates being consequently internal salts. Similar behaviour is shown by the amino-acids towards copper and nickel salts; the *α*-acids yield salts which are abnormal in colour and in electrolytic dissociation, whereas the *β*- and *γ*-acids, in which the amino-group is further removed from the carboxyl group, yield normal nickel and copper salts (compare Callegari, A., 1906, i, 937; Tschugaev and Serbin, A., 1911, i, 115).

Ammonium vanadylsalicylate, $+3H_2O$, is prepared by reduction of metavanadic acid by means of sulphur dioxide and treatment with ammonium salicylate. The *potassium* ($+3H_2O$), *calcium* ($+3H_2O$), and *thallium* (anhydrous) salts were also prepared. T. H. P.

Aromatic Nitro-derivatives. III. Dinitromethoxybenzoic and Dinitroaminobenzoic Acids. Michele Giua (*Gazzetta*, 1915, **45**, i, 352—358. Compare this vol., i, 885).—The action of potassium hydroxide (2 mols.) in methyl-alcoholic solution on 2 : 3 : 4- and 2 : 4 : 5-trinitrobenzoic acids yields 2 : 4-dinitro-3-methoxybenzoic and 4 : 6-dinitro-3-methoxybenzoic acids, whilst that of alcoholic ammonia on these trinitro-acids under ordinary conditions gives 2 : 4-dinitro-3-aminobenzoic and 4 : 6-dinitro-3-aminobenzoic acids.

2 : 4 : 5-Trinitrobenzoic acid is more stable than the 2 : 3 : 4-acid, but, when heated slightly above its melting-point, either acid liberates carbon dioxide. With small quantities of these acids, such as the amount contained in an ordinary melting-point tube, this reaction proceeds easily, but with 0·2—0·5 gram of substance, decomposition occurs, and when about 1 gram is heated in a vacuum distillation apparatus, a violent explosion takes place.

2 : 4-*Dinitro*-3-*methoxybenzoic acid*, $C_8H_6O_7N_2$, crystallises in long, slightly yellow needles, turning brown at 235°, m. p. 240—241°, and gives a pale yellow coloration with alkali in the hot; its *silver* and *potassium* salts were prepared.

4 : 6-*Dinitro*-3-*methoxybenzoic acid* forms white needles, m. p. 186—187°, and gives a pale yellow coloration with alkali in the hot; its *potassium* salt was prepared.

4 : 6-*Dinitro*-3-*aminobenzoic acid*, $C_7H_5O_6N_3$, forms masses of yellow needles with a reddish lustre, m. p. 270° (decomp.), and gives an intense wine-red coloration with alkalis. Its *ammonium*, *silver* ($+H_2O$), and *potassium* salts were prepared.

Ammonium 2 : 4-*dinitro*-3-*aminobenzoate*, $C_7H_4O_6N_3{\cdot}NH_4$, forms yellow needles, m. p. about 240° (decomp.). T. H. P.

Behaviour of *p*-Dimethylamino-*o*-benzoylbenzoic Acid and Related Substances towards Nitrous Acid. Otto Fischer and Hans Loewe (*J. pr. Chem.*, 1915, [ii], **92**, 54—60).—The compounds obtained by Limpricht (A., 1898, i, 435) by the action of nitrous acid on 2-*p*-dimethylaminobenzoylbenzoic acid, 2 : *p*-dimethylaminobenzylbenzoic acid, and *p*-dimethylaminophenylphthalide are not nitroso compounds, but the corresponding nitro-derivatives.

Nitro-2-*p*-dimethylaminobenzoylbenzoic acid has m. p. 164° (compare Limpricht, A., 1899, i, 815).

2-*p*-Dimethylaminobenzylbenzoic acid is readily prepared by reducing 2-*p*-dimethylaminobenzoylbenzoic acid with zinc dust and glacial acetic acid containing a little fuming sulphuric acid. With nitrous acid, it yields a *nitro*-derivative, long, stout, orange-red, pointed prisms, m. p. 133—134°, together with a *substance*, m. p. about 180°.

The action of nitrous acid on *p*-dimethylaminophenylphthalide gives rise to a *nitro*-derivative, lustrous, thin, orange-red leaflets, m. p. 157°, which is accompanied by p-*nitrosomethylaminophenylphthalide*,

$$C_6H_4\langle\begin{matrix}O\text{---}\\CO\end{matrix}\rangle CH{\cdot}C_6H_4{\cdot}NMe{\cdot}NO,$$

pale yellow needles or prisms, m. p. 175°. F. B.

Alkyl Ethers of Certain Oximes. IV. Luigi Alessandri (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 347—352).—Experimental details are given of the work already published (this vol., i, 412).

The *O*-methyl ether of benzophenoneoxime forms colourless, tabular or prismatic crystals, m. p. 60°, and yields α-methylhydroxylamine on hydrolysis with alcoholic hydrochloric acid. T. H. P.

Natural Musk. Erwin Sack (*Chem. Zeit.*, 1915, **39**, 538).—An odorous constituent different from muscone (compare A., 1906, i, 525, 595) was isolated from natural musk by the following process: the substance was boiled for several hours with alcoholic potassium hydroxide solution, the alcohol then evaporated, and the solution extracted with ether. The residue obtained on evaporating the ethereal extract was distilled with steam to remove scatole, again extracted with ether, the ether evaporated, and the residue dissolved in alcohol. The alcoholic solution, after filtration, was evaporated, and the oily residue obtained converted into a *semicarbazone*, $C_{18}H_{33}ON_3$; the latter, after being washed with light petroleum, crystallised from alcohol in plates, m. p. 187°. The *ketone*, $C_{17}H_{30}O$, separated from the semicarbazone, had m. p. 32·5° and b. p. 204—205°/17 mm. or 342°/741·5 mm., and yielded an *oxime*, m. p. 92°. The name *civetone* (*zibetone*) is given to the substance. W. P. S.

Acetotriketohexamethylene [Acetyl*cyclo*hexanetrione]. GUSTAV HELLER (*Ber.*, 1915, **48**, 1286—1288).—The substance described as phloracetophenone by Leuchs and Sperling (this vol., i, 141) and by Hoesch (this vol., i, 821) is identical with the acetyl*cyclo*hexanetrione of the author (A., 1912, i, 274), the discrepancy in m. p. being due to impurity in the last product. From the chemical behaviour of the substance it is held that the constitution must be that of acetyl*cyclo*hexanetrione. D. F. T.

Auto-oxidations in the Light in the Terpene Series. E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 850—854. Compare this vol., i, 826).—Five grams of citronellaldehyde and 100 c.c. of water were exposed to the light for about four months in a 3-litre flask filled with oxygen. The aldehyde disappeared almost entirely, the products obtained being: acetic acid; a heptoic, probably β-methylhexoic, acid; menthone; *iso*pulegol; acetone; β-methyladipic acid; dihydroxycitronellic acid; and a small proportion of a ketone, $C_{10}H_{18}O$, which gives a *semicarbazone*, m. p. 206—207°, and does not appear to be identical with any of the known ketones of the terpene series. T. H. P.

Esters of Silicic Acid. GIOVANNI PELLINI (*Gazzetta*, 1915, **45**, i, 380—385).—Treatment of the compound $Si(OEt)_3Cl$ with dry silver oxide (compare Madsen, A., 1913, ii, 136) yields ethyl diorthosilicate, but, under similar conditions, neither $Si(OEt)_2Cl_2$ nor $Si(OEt)Cl_3$ gives a product of constant composition.

l-*Bornyl silicate*, $Si(O\cdot C_{10}H_{17})_4$, obtained by the interaction of silicon tetrachloride (1 mol.) and *l*-borneol (4 mols.) in light petroleum, forms a white, crystalline mass, m. p. 291—292°; in a 13·006% solution in toluene it has D_4^{20} 0·8827 and $[\alpha]_D^{20}$ − 41·55°, and in 16·823% solution, D_4^{20} 0·8878, $[\alpha]_D^{20}$ − 42·88°.

Tri-l-*bornyl chlorosilicate*, $Si(O\cdot C_{10}H_{17})_3Cl$, similarly obtained, forms transparent, colourless crystals, m. p. 215—218°, and in a 16·527% solution in toluene it has D_4^{20} 0·8905, $[\alpha]_D$ − 36·72°.

Di-l-*bornyl dichlorosilicate*, $Si(O\cdot C_{10}H_{17})_2Cl_2$, forms a colourless liquid, b. p. 203—205°/10 mm., $D_4^{25\cdot4}$ 1·0926, $[\alpha]_D^{25\cdot4}$ − 30·34°, which sets to a white, crystalline mass at temperatures not exceeding 20°.

l-*Bornyl trichlorosilicate*, $Si(O\cdot C_{10}H_{17})Cl_3$, obtained, like the preceding compound, from silicon tetrachloride and *l*-borneol in absence of solvent, is a liquid, b. p. 140—142°/760 mm., $D_4^{24\cdot9}$ 1·1885, $[\alpha]_D^{24\cdot9}$ − 20·09°.

l-*Bornyl dimetasilicate*, $Si_2(O\cdot C_{10}H_{17})_2O_3$, prepared by the action of excess of silver oxide on *l*-bornyl trichlorosilicate, forms vitreous scales, softening at about 92°, m. p. 135—140°. T. H. P.

The Decomposition of β-Nataloin and β-Homonataloin. E. LÉGER (*Compt. rend.*, 1915, **161**, 133—135*).—On submitting β-nataloin (compare A., 1914, i, 309, 707) to repeated crystallisation, crystals were obtained having $[\alpha]_D$ − 146·5°, equal to that of natural nataloin. The mixture of crystals obtained from the mother liquors of this process had $[\alpha]$ − 15°, and these on crystallisation gave an aloin

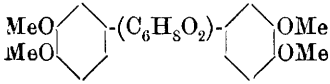
* and *J. Pharm. Chim.*, 1915, [vii], **12**, 224—228.

having $[\alpha]_D + 63°$, whilst the mother liquors yielded a fraction having $[\alpha]_D - 145°$. All efforts to increase the rotatory power of the *d*-aloin were unsuccessful. β-Nataloin is therefore probably a racemic compound, and unsuccessful attempts were made to obtain it pure and inactive. This decomposition into *d*- and *l*-nataloins was much more rapid on precipitation from alcoholic solution by the addition of water.

β-Homonataloin, having $[\alpha]_D + 8°$, was also decomposed by precipitation with water from an alcoholic solution into a compound having $[\alpha]_D + 63°$, which could not be further decomposed, and into a compound having $[\alpha]_D - 147{\cdot}6°$, which corresponds with natural homonataloin. β-Homonataloin is thus also a racemic compound, capable of being resolved by suitable methods of crystallisation.

W. G.

Eudesmin and its Derivatives. Robert Robinson and Henry G. Smith (*J. Roy. Soc., New South Wales*, 1914, **48**, 449—463).—Eudesmin, $C_{22}H_{26}O_6$, occurs in the kinos of eucalyptus species, the oils of which are characterised by the absence of phellandrene, and the presence of cineole and pinene. It was isolated by extracting a syrupy aqueous solution of the kino with ether, and purified by treatment with chloroform and crystallisation from methyl alcohol. It forms colourless, prismatic needles, m. p. 107°, $[\alpha]_D^{21} - 64{\cdot}4°$ (in chloroform solution). Eudesmin contains four methoxy-groups, and was unacted on by hydroxyl or ketone reagents. It dissolved in sulphuric acid to a red solution, and was converted by nitric acid into *dinitroeudesmin*, colourless, slender needles, m. p. 214°. Boiling with concentrated nitric acid converted it into 4 : 5-dinitroveratrole (2 mols.). *Dichloroeudesmin* was obtained by the action of chlorine on eudesmin in acetic acid solution. It formed colourless, rectangular plates, m. p. 163°. *Dibromoeudesmin*, prepared in a similar manner, formed colourless needles, m. p. 172°, $[\alpha]_D^{22} + 69{\cdot}4°$ (in chloroform), which on oxidation with permanganate gave 6-bromoveratric acid, m. p. 184°, identical with the acid obtained by the hydrolysis of the product of bromination of methyl veratrate. *Di-iodoeudesmin*, prepared by the action of iodine monochloride, formed needles, m. p. 175°. The production of veratrole and veratric acid derivatives from eudesmin points to the presence in it of the structure of the annexed type.



The constitution of the central group is at present undetermined, but the authors suggest two closed five-membered carbon-oxygen chains as the most probable structure.

G. F. M.

Phenol-Blue. Gustav Heller (*Ber.*, 1915, **48**, 1288—1289).—A weakness is indicated in Mohlau's method for the preparation of phenol-blue (compare Wieland, this vol., i, 848), and Gnehm's method is stated to give a pure product (Heller, A., 1912, i, 916). *as-p*-Phenylenedimethyldiamine can be obtained by reduction of nitrosodimethylaniline hydrochloride in aqueous solution by zinc dust at 40° without the addition of acid.

D. F. T.

Nitro-derivatives of Dinaphthathioxin. Brojendra Nath Ghosh and Samuel Smiles (T., 1915, **107**, 1144—1148).—The direct nitration of dinaphthathioxin or of *iso*dinaphthathioxin yields the dinitro-derivative of the oxide, but the results are unsatisfactory. The authors have obtained the desired nitro-compounds by reducing these dinitro-oxides to the thio-derivatives by hydrogen chloride or similar reagents; the product obtained depends on the nature of the substituents present and on the experimental conditions.

Chloronitrodinaphthathioxin oxide, $C_{10}H_5Cl<^{SO}_{O-}>C_{10}H_5\cdot NO_2$, yellow prisms, m. p. 268° (decomp.), obtained by triturating chloronitrodinaphthathioxin with nitric acid, D 1·42, is reduced to the original chloronitrodinaphthathioxin by boiling it with an excess of acetyl chloride and a small quantity of phenyl acetate. In a similar manner, *dinitrodinaphthathioxin,* orange prisms, m. p. above 300°, and *dinitro*-iso*dinaphthathioxin,* orange prisms, m. p. 274—275°, have been prepared.

Nitroacetoxydinaphthathioxin, $NO_2\cdot C_{10}H_5<^{S}_{O}>C_{10}H_5\cdot OAc$, red needles, m. p. 245—246°, obtained by heating mononitronaphthasulphonium-quinone (T., 1914, **105**, 1746) suspended in acetic anhydride, containing camphorsulphonic acid, has not been successfully converted into the oxide. C. S.

The Alkaloids of the Calabar Bean. I. Eserine. Max Polonovski (*Bull. Soc. chim.*, 1915, [iv], **17**, 235—244. Compare Petit and Polonovski, A., 1894, i, 264; Salway, T., 1912, **101**, 978).—The author has prepared a number of derivatives from eserine with a view to throw further light on its constitution. With methyl iodide in anhydrous benzene it yields a *methiodide,* m. p. 120—125° (decomp.). On passing sulphur dioxide into a solution of eserine in ethyl ether its *sulphite,* m. p. 106° (decomp.), is obtained as a white, crystalline powder. In solution in water this has $[\alpha]_D + 20°$. On passing sulphur dioxide into this aqueous solution it becomes more and more yellow, and the rotation rises to $[\alpha]_D + 87·6°$, and this solution, evaporated to dryness in the air, leaves a residue of *eserine sulphate.* When the latter salt is dissolved in water it has $[\alpha]_D - 93·9°$, but if its solution is saturated with sulphur dioxide it has $[\alpha]_D + 87·6°$, and the solution becomes yellow.

Eserine is readily decomposed by sodium ethoxide in absolute alcohol, giving eseroline and methyl-urethane. Eseroline yielded a *sulphate,* m. p. 202—203°, which in water or dilute sulphuric acid had $[\alpha]_D - 164°$ (calculated on the base).

When eserine is treated with ethyl toluenesulphonate in absolute alcohol in the presence of sodium ethoxide it yields an ether, not of eserine, but eseroline, to which the name *eserethole* has been given. It is also readily obtained by the same process from eseroline, and is a colourless liquid, b. p. 308—310°, $[\alpha]_D - 81°$. It is strongly alkaline to litmus, and yields a *hydrobromide,* colourless prisms, m. p. 178°, and a *picrate,* m. p. 133°. When warmed with alkalis it gives no trace of

methylamine. Eserethole gives a *methiodide*, colourless plates, m. p. 171°, which is decomposed by alkalis, giving a *base*, m. p. 80°.

With methylcarbimide, eseroline yields a *compound*, m. p. 195—196°, which seems to be isomeric with eserine, and is decomposed by aqueous barium hydroxide, giving carbon dioxide, methylamine, and eseroline. With phenylcarbimide, eseroline yields a *compound*, m. p. 184°, and an oil. W. G.

The Alkaloids of the Calabar Bean. II. Geneserine, a New Alkaloid of the Bean. MAX POLONOVSKI and CHARLES NITZBERG (*Bull. Soc. chim.*, 1915, [iv], **17**, 244—256).—By the extraction of Calabar beans with ether, or by soaking them in 2% sodium hydroxide and then extracting with ether, a new alkaloid, *geneserine*, has been isolated. It is obtained in orthogonal crystals, m. p. 128—129°, having $[\alpha]_D$ −175° in alcohol and −188° in dilute sulphuric acid. It is a feeble base, but does not give crystalline salts with mineral acids. It yields a *salicylate*, m. p. 82—90°, a *picrate*, m. p. 175°, and a *methiodide*, m. p. 215°. When treated with alkalis, geneserine reddens, but less readily than eserine. On heating to 160°, it decomposes, giving off methylcarbimide. This is also evolved on oxidation in acid media with potassium permanganate or chromic acid. Geneserine unites with iodine and bromine more readily than eserine, giving a periodide and a perbromide. It reduces silver nitrate solution in the cold, forming a silver mirror. When treated with alkalis, it yields methylamine and the alkali carbonate, a quantitative estimation of these two products indicating the presence of the group ·CO·NHMe in geneserine.

Like eserine, geneserine is decomposed by sodium in absolute alcohol, and gives *geneseroline*, $C_{13}H_{18}O_2N_2$, m. p. 150°; $[\alpha]_D$ −176° in alcohol and −230° in dilute sulphuric acid. It gives a *picrate*, m. p. 175°; a *hydrobromide*, m. p. 208°; a *hydrochloride*, m. p. 154°; a normal *sulphate*, m. p. 160°; and an *acid sulphate*, m. p. 183—184°.

When geneserine is treated with either ethyl bromide or ethyl toluenesulphonate in absolute alcohol in the presence of sodium, *geneserethole*, $C_{15}H_{22}O_2N_2$, is obtained in plates, m. p. 83°, $[\alpha]_D$ −182° in alcohol. It gives a *picrate*, m. p. 156—157°; a *hydriodide*, m. p. 108°, and a *hydrochloride*, m. p. 120—124°. With methyl iodide, geneserethole yields an *iodo-compound*, m. p. 225°; a *methiodide*, m. p. 140°, which is not decomposed by alkalis; and another *methiodide*, m. p. 214°, which with alkalis yields a quaternary *base*, which also gives a *methiodide*, m. p. 129°, not decomposed by alkalis, but decomposed by silver hydroxide, giving a new quaternary *base*, which yields a *methiodide*, m. p. 120°. Geneserethole is also readily obtained by the action of ethyl bromide on geneseroline in the presence of sodium ethoxide. If ethyl toluenesulphonate is used, the main product in this case is eserethole, and but a trace of geneserethole is formed.

Geneserine is reduced by zinc dust in alcohol acidified with acetic acid to eserine. If zinc and sulphuric acid are used, a *substance* is obtained, non-crystalline, and having $[\alpha]_D$ −54° in sulphuric acid. If sulphur dioxide is passed through the aqueous solution of any salt of geneserine, eserine is obtained together with a *sulphonated derivative*

of eserine, m. p. 176°. Geneseroline and geneserethole are similarly readily reduced to eseroline and eserethole respectively.

Geneserine, unlike eserine and physovenine, has no appreciable myotic action. W. G.

Strychnine and Brucine. R. Ciusa and L. Vecchiotti (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 480—483).—The compound,

$$C_{23}H_{28}O_2N_2Br_4,$$

obtained by the action of bromine on *iso*strychnine in acetic acid solution and treatment with boiling alcohol of the perbromide thus formed (compare Ciusa and Scagliarini, A., 1912, i, 798), is now shown to be the hydrobromide of a base.

The free *base*, $C_{20}H_{21}NBr_3(:NH)\cdot CO_2Et$, forms minute, colourless needles, and decomposes without melting. Its *aurichloride*,

$$C_{23}H_{27}O_2N_2Br_3,HAuCl_4,$$

forms slightly soluble, yellow needles, and its hydrobromide exerts a physiological action similar to that of strychnine.

When *iso*strychnine hydrobromide is heated in a sealed tube with alcoholic hydrobromic acid, it yields the crystalline hydrobromide of a bromo-compound, to be described later.

Decomposition of *iso*strychnine perbromide with dilute sodium carbonate (*loc. cit.*) and then with dilute ammonia yields the *hydrobromide*, $(C_{20}H_{21}NBr_3)\begin{matrix}CO\\ |\\ N\end{matrix}$, $HBr + H_2O$, which forms yellow scales.

Cacotheline (bidemethylnitrobrucine hydrate) yields a *dioxime*,

$$C_{21}H_{21}O_6N_5,3\tfrac{1}{2}H_2O,$$

which forms golden-yellow needles, m. p 319—320°, and deflagrates at a higher temperature; this appears to be the dioxime of a diketone, $C_{21}H_{19}O_4N_3(:O)_2$, which contains $1H_2O$ less than the base of cacotheline. T. H. P.

Bases Formed by the Alkylation of Pyrroles. G. Plancher and Bruno Tanzi (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 412—417).—In all their properties, the bases obtained by alkylation of pyrroles exhibit close analogy with the indolenines, but no direct proof exists that they are derived from the penta-atomic nucleus, pyrrolenine or methylenepyrroline. A further number of pyrroles have now been alkylated by the action of alkyl haloids on magnesium pyrryl salts.

By the action of ethyl iodide on magnesium 2 : 3 : 5-trimethylpyrryl bromide, Hess and Wissing (A., 1914, i, 725) obtained a base, $C_8H_{13}N$, which they regarded as a trimethyldihydropyridine. The authors find, however, that this base has the formula $C_9H_{15}N$, and that its properties are perfectly similar to those of its analogues obtained previously or described in the present paper. Further, the products of Oddo and Mameli's reaction (A., 1914, i, 80) contain a base, $C_7H_{11}N$, which is also similar to others prepared in this way.

The action of *iso*propyl iodide on magnesium 2 : 5-dimethylpyrryl iodide yields: (1) 2 : 5-*dimethyl*-3-iso*propylpyrrole*, $C_9H_{15}N$, b. p. 216—217°. For purposes of comparison, 2 : 5-dimethyl-1-*iso*propylpyrrole was prepared in the following way: ethyl 2 : 5-dimethyl-1-*iso*propylpyrrole-3 : 4-dicarboxylate was obtained by condensation of

ethyl diacetylsuccinate with *iso*propylamine in acetic acid solution, and the corresponding *dicarboxylic acid*, $C_{11}H_{15}O_4N$, which decomposes at about 200°, converted into 2 : 5-*dimethyl*-1-iso*propylpyrrole*, b. p. 182—183°, by distillation; (2) A basic mixture which gives two isomeric *picrates*, $C_{12}H_{21}N,C_6H_3O_7N_3$, m. p. 173—174° and 107°, probably corresponding with the two dimethyldi*iso*propylpyrrolenines,

$$N\!\leqslant\!\begin{matrix}CMe\cdot CPr^{\beta}{}_2\\ CMe{:}CH\end{matrix} \quad \text{and} \quad N\!\leqslant\!\begin{matrix}CMe\text{---}CH\\ \|\quad\ \ |\\ CMePr^{\beta}\cdot CPr^{\beta}\end{matrix}.$$

The action of *iso*propyl iodide on magnesium tetramethylpyrryl iodide yields an oily *base*, probably

$$N\!\leqslant\!\begin{matrix}CMe\cdot CMePr^{\beta}\\ CMe{:}CMe\end{matrix} \quad \text{or} \quad N\!\leqslant\!\begin{matrix}CMe\text{---}CMe\\ \|\quad\ \ |\\ CMePr^{\beta}\cdot CMe\end{matrix},$$

which forms a crystalline hydrochloride and a *picrate*, m. p. 152—153°.

The action of methyl iodide on magnesium pyrryl bromide yields, in addition to pyrrolic products (compare Oddo and Mameli, *loc. cit.*), a *base*, $C_7H_{11}N$, which has an odour of mint and is probably the trimethylpyrrolenine, $N\!\leqslant\!\begin{matrix}CH\text{---}CH\\ \|\quad\ \ |\\ CMe_2\cdot CMe\end{matrix}$ or $N\!\leqslant\!\begin{matrix}CMe\cdot CMe_2\\ CH{=}CH\end{matrix}$; it forms a *picrate*, m. p. 218—219°.

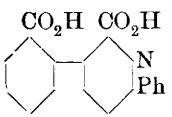
The *base*, $C_9H_{15}N$, b. p. 180°/768 mm., obtained from ethyl iodide and magnesium 2 : 3 : 5-trimethylpyrryl iodide (*vide supra*), forms a *picrate*, m. p. 199—200°, and has the structure

$$N\!\leqslant\!\begin{matrix}CMe\cdot CMeEt\\ CMe{:}CH\end{matrix} \quad \text{or} \quad N\!\leqslant\!\begin{matrix}CMe\text{---}CH\\ \|\quad\ \ |\\ CMeEt\cdot CMe\end{matrix};$$

the mother liquor yields a small proportion of another *picrate*, m. p. 148—149°.

The action of methyl iodide on magnesium 2-methyl-5-*iso*propylpyrryl iodide yields besides methyl*iso*propylpyrrole and its higher homologues, *trimethyliso*propylpyrrolenine, $C_{10}H_{17}N$, for which four formulæ are possible; its *picrate*, m. p. 121—122°, was prepared. T. H. P.

Doebner's Reaction. I. R. Ciusa (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 262—265).—Doebner and Kuntze (A., 1889, 411; see also Doebner, A., 1894, i, 261, 532) showed that the action of a primary aromatic amine on a mixture of an aldehyde with pyruvic acid yields a cinchonic acid. The β-naphthacinchonic acids obtained in this way from β-naphthylamine may be derivatives of either anthracene or phenanthrene, the phenanthrenic structure, although not definitely established, being the one usually accepted, especially since the publication of Marckwald's investigations on quinolinic condensations ("Die Benzoltheorie"; A., 1893, i, 603; 1894, i, 474). This structure is now confirmed by the author, who has obtained, by oxidation of α-phenyl-β-naphthacinchonic acid, an acid giving analytical numbers corresponding with diphenylpyridinedicarboxylic acid (annexed formula).



In Doebner's reaction, a molecule of hydrogen is eliminated, and it has been shown (A., 1913, i, 681) that, in the preparation by this method of α-phenyl-β-naphthacinchonic and α-*p*-dimethylaminophenyl-β-naphthacinchonic acids, hydrogenated derivatives of these acids are also obtained. That

these secondary products are formed by the reduction of the fundamental cinchonic acid is shown by the following properties: (1) they dissolve in solutions of alkali hydroxides or carbonates or ammonia; (2) with methyl sulphate in alkaline solution they readily yield methyl esters; (3) by alkaline permanganate they are converted into the principal products of the reaction; (4) by distillation with soda lime they yield the same naphthaquinoline derivatives as the non-hydrogenated products (compare succeeding abstract). T. H. P.

Doebner's Reaction. II. R. Ciusa and G. Buogo (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 265—270).—The experimental results of the work described in the preceding paper are given.

Diphenylpyridinedicarboxylic acid, $C_{19}H_{13}O_4N$, forms a white, crystalline powder, m. p. 198°, and yields transparent crystals containing $1C_6H_6$, m. p. 195°. Its *silver* salt is a white powder which rapidly blackens.

The reduction products obtained together with 2-phenyl-β-naphthacinchonic acid consist of a mixture of the di- and tetra-hydrogenated acids, m. p. 226°; the methyl ester has m. p. 134°. The *2-phenyltetrahydro-β-naphthacinchonic acid*, $C_{20}H_{17}O_2N$, which forms small, white scales, m. p. 232°, remains undissolved when the mixed acids are treated with benzoyl chloride; its *sodium* salt was prepared. Treatment of the crude methyl ester of the hydrogenated acids with benzoyl chloride yields the *benzoyl* derivative of *methyl 2-phenyltetrahydro-β-naphthacinchonate*, $C_{28}H_{23}O_3N$, which crystallises in colourless scales, m. p. 211°, and, on hydrolysis by means of 7% alcoholic potassium hydroxide, gives the *benzoyl* derivative of *2-phenyltetrahydro-β-naphthacinchonic acid*, $C_{27}H_{21}O_3N$, in colourless needles, m. p. 221°.

2-p-*Dimethylaminophenyldihydro-β-naphthacinchonic acid*, $C_{22}H_{20}O_2N_2 + \frac{1}{2}H_2O$, m. p. 275°, obtained as a yellow, gelatinous substance, was purified by solution in dilute ammonia solution and precipitation by means of dilute acetic acid. T. H. P.

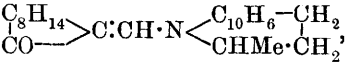
Resolution of Externally Compensated Tetrahydro-β-naphthaquinaldine into its Optically Active Components. Charles Stanley Gibson and John Lionel Simonsen (T., 1915, **107**, 1148—1159).—The application of Pope and Peachey's equilibrium method (T., 1893, **73**, 893) to the resolution of *dl*-tetrahydro-β-naphthaquinaldine (2 equiv.) by ammonium *d*(or *l*-)-α-bromocamphor-π-sulphonate (1 equiv.) in the presence of hydrochloric or sulphuric acid leads to a successful result, but large quantities of the pure salts cannot be conveniently obtained, as the two salts, *dAdB* and *dAlB* (or *lAlB* and *lAdB*), are crystalline in the presence of each other, and have only slightly differing solubilities. Attempts to resolve the *dl*-base by *d*-hydroxymethylenecamphor were unsuccessful.

dl-Tetrahydro-β-naphthaquinaldine forms a *picrate*, yellow needles containing $2H_2O$, m. p. 100—101°.

d-*Tetrahydro-β-naphthaquinaldine* d-*α-bromocamphor-π-sulphonate*, $C_{14}H_{15}N,C_{10}H_{14}OBr\cdot SO_3H$, colourless plates, begins to decompose at 233°, melts completely at 240°, and has $[\alpha]^{29\cdot30}_{5461}$ +134·7° in ethyl alcohol. The *lAlB-salt* behaves similarly, and has $[\alpha]^{29\cdot30}_{5461}$ −134·5° in ethyl alcohol. The *dAlB-salt* has $[\alpha]^{29\cdot30}_{5461}$ +20·6° in ethyl alcohol.

The bases are liberated by sodium hydroxide solution. d-*Tetrahydro-β-naphthaquinaldine* and the l-*base* form colourless prisms, m. p. 54·6°. The former has $[\alpha]^{29-30}_{5461}$ +109·04° in ethyl alcohol and +157·0° in benzene, and forms a *platinichloride*, orange-red, microcrystalline powder, decomp. about 200°, and a *benzoyl* derivative, colourless needles, m. p. 198—199°, $[\alpha]^{29-30}_{5461}$ −587·0° in ethyl alcohol. The l-*base* has $[\alpha]^{29-30}_{5461}$ −108·5° in ethyl alcohol, and forms a *benzoyl* derivative, colourless needles, m. p. 198—199°, $[\alpha]^{29-30}_{5461}$ +587·6° in ethyl alcohol.

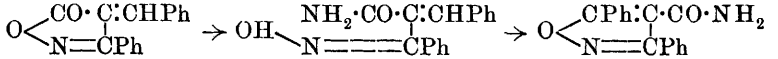
dl-*Tetrahydro-β-naphthaquinaldino*-d-*methylenecamphor*,



colourless plates, m. p. 182—183°, prepared by the condensation of its components in the presence of acetic acid, has $[\alpha]^{29-30}_{5461}$ +413·2° in ethyl alcohol, +351·2° in benzene, and +415·3° in glacial acetic acid, and yields *d*-bromo-oxymethylenecamphor and dl-*tetrahydro-β-naphthaquinaldine hydrobromide*, m. p. above 245°, by treatment with bromine and alcohol. C. S.

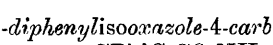
Phenylquinolinein, a Heterocyclic Analogue of Phenolphthalein. ARTHUR W. DOX (*J. Amer. Chem. Soc.*, 1915, **37**, 1948—1949).—Quinolinic anhydride condenses with phenol in the presence of sulphuric acid to form *phenolquinolinein*, $C_{18}H_{13}O_4N$, as a yellow, granular substance with similar indicator properties to phenolphthalein. J. C. W.

Spontaneous Oxidations in Presence of Aldehydes. MARIO BETTI (*Gazzetta*, 1915, **45**, i, 362—371. Compare Betti and Alessandri, this vol., i, 713).—It has been previously shown (A., 1906, i, 985; 1907, i, 854) that, in ammoniacal solution and in presence of atmospheric oxygen, 1-phenyl-4-benzylidene-3-methyl-5-pyrazolone undergoes spontaneous oxidation into rubazonic acid, the oxidation being favoured by the catalytic action of the benzaldehyde, which becomes detached from the pyrazolone derivative. This reaction has now been extended to the analogous 3-phenyl-4-benzylidene*iso*-oxazolone, but, with this compound in alcoholic ammonia, the reaction proceeds in a totally different manner, and gives a satisfactory yield only when a little free benzaldehyde is added. The product obtained, namely, the amide of 3 : 5-diphenyl*iso*oxazole-4-carboxylic acid, apparently results from the atmospheric oxidation of an intermediate amide :



By treatment with concentrated sodium hydroxide, the final amide is converted into 3 : 5-diphenyl*iso*oxazole-4-carboxylic acid, and this, by heating, into 3 : 5-diphenyl*iso*oxazole (compare Goldschmidt, A., 1896, i, 189). The structure of 3 : 5-diphenyl*iso*oxazole-4-carboxylic acid is confirmed by the preparation of its ethyl ester by the interaction of hydroxylamine and ethyl dibenzoylacetate (compare Claisen, A., 1894, i, 32).

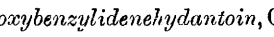
The *amide* of 3 : 5-*diphenylisooxazole*-4-*carboxylic acid*,



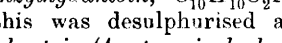
forms pale, straw-yellow, cubic or prismatic crystals, m. p. 229—230° (decomp.). The free *acid*, $C_{16}H_{11}O_3N$, forms small, shining, white cubes or rhombohedra, m. p. 233°. The *sodium* salt was analysed, and the *silver*, *barium*, *copper*, *mercuric*, *lead*, and *ferric* salts prepared. The *ethyl* ester, $C_{18}H_{15}O_3N$, forms shining, highly refractive prisms, m. p. 51—52°. T. H. P.

Hydantoins. XXXI. A New Synthesis of *o*-Tyrosine. Treat B. Johnson and Walter Moody Scott (*J. Amer. Chem. Soc.*, 1915, **37**, 1846—1856).—The condensations of hydantoins with aldehydes have now been extended to salicylaldehyde and its methyl ether, and by this means the "hydantoin method" of synthesising α-amino-acids has been applied to the preparation of *o*-tyrosine and its methyl ether.

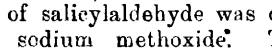
2-Thiohydantoin (A., 1912, i, 53) was heated with salicylaldehyde, anhydrous sodium acetate, and acetic acid for four hours at 140—150°, when 2-*thio*-4-*o*-*hydroxybenzylidenehydantoin*, , was obtained in almost theoretical yield, as radiating needles, m. p. 248°. This was desulphurised by heating with an approximately 25% solution of monochloroacetic acid at 140—150°. 4-*o*-*Hydroxybenzylidenehydantoin*, $C_{10}H_8O_3N_2$, was thus obtained, in short needles, m. p. 271° (decomp.), but it could not be obtained readily by the application of hydantoin itself in the first reaction. The above thiocompound was also reduced by means of sodium amalgam at 75° to 2-*thio*-4-*o*-*hydroxybenzylhydantoin*, $C_{10}H_{10}O_2N_2S$, rosettes of needles, m. p. 107°, and this was desulphurised as above. The product, 4-*o*-*hydroxybenzylhydantoin* (4-*o*-*tyrosinehydantoin*),



crystallised in clusters of stout prisms, m. p. 205—206°, and could also be obtained by reducing the above 4-*o*-hydroxybenzylidenehydantoin. The hydantoin was hydrolysed by concentrated barium hydroxide to *o*-tyrosine, which decomposed, when quickly heated, at 247—250° (hydrochloride, decomp. 180°).

The methyl ether of salicylaldehyde was obtained by the action of methyl iodide and sodium methoxide. This condensed with 2-thiohydantoin to give 2-*thio*-4-*o*-*methoxybenzylidenehydantoin*, m. p. 227°, and with hydantoin itself to give a small yield of 4-*o*-*methoxybenzylidenehydantoin*,  , m. p. 178°. The latter was more conveniently prepared by desulphurising the thiocompound. It was reduced by sodium amalgam to *o*-*methoxybenzylhydantoic acid* [α-*carbamido*-β-*o*-*methoxyphenylpropionic acid*],

$$OMe\cdot C_6H_4\cdot CH_2\cdot CH(NH\cdot CO\cdot NH_2)\cdot CO_2H,$$

rectangular prisms, m. p. 189°, which was condensed to 4-*o*-*methoxybenzylhydantoin*,  , m. p. 186°, by boiling

with dilute hydrochloric acid. Either of these compounds was easily hydrolysed by barium hydroxide to *o-methoxyphenylalanine*, $OMe\cdot C_6H_4\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, rosettes of needles, m. p. 206°. This amino-acid was condensed with ammonium thiocyanate and acetic anhydride to *2-thio-3-acetyl-4-o-methoxybenzylhydantoin*, $CS<^{NH-CO}_{NAc\cdot CH\cdot CH_2\cdot C_6H_4\cdot OMe}$, m. p. 168°, which was hydrolysed by hydrochloric acid to *2-thio-4-o-methoxybenzylhydantoin*, m. p. 190°, and this was also obtained by reducing the above 2-thio-4-*o*-methoxybenzylidenehydantoin. J. C. W.

Hydantoins. XXXII. Synthesis of the Hydantoin of 5-Amino-2-hydroxyphenylalanine. Treat B. Johnson and Walter M. Scott (*J. Amer. Chem. Soc.*, 1915, **37**, 1856—1863). —The hydantoins of aminophenylalanine derivatives are of particular interest because it may be possible to convert them, through the diazo-reaction, into α-amino-acids which are otherwise almost impossible of synthesis. Such an acid, for example, is 2 : 5-dihydroxyphenylalanine, $C_6H_3(OH)_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, which is of interest because it is most probably an intermediate compound in the formation of homogentisic acid from tyrosine and phenylalanine in cases of alcaptonuria. The present paper describes the hydantoin of this acid, but the final hydrolysis could not be achieved. It may be possible to obtain the dimethyl ether, however, and to demethylate that, and experiments in this direction are in progress.

Gentisaldehyde, obtained by oxidising salicylaldehyde (Neubauer and Flatow, A., 1907, i, 772), was condensed with 2-thiohydantoin, and the product, *2-thio-4-om'-dihydroxybenzylidenehydantoin*,

$$CS<^{NH\cdot CO}_{NH\cdot C:CH\cdot C_6H_3(OH)_2}$$

decomp. 270°, was desulphurised by means of chloroacetic acid.

4-om'-*Dihydroxybenzylidenehydantoin*, $C_{10}H_8O_4N_2$, decomp. above 300°, is so unstable in alkaline solution that it could not be reduced to the benzyl compound.

5-Nitro-2-hydroxybenzaldehyde, prepared from salicylaldehyde, condensed with 2-thiohydantoin to form *2-thio-4-m'-nitro-o-hydroxybenzylidenehydantoin*, $CS<^{NH\cdot CO}_{NH\cdot C:CH\cdot C_6H_3(OH)\cdot NO_2}$, not melted below 300°, and this was desulphurised to *4-m'-nitro-o-hydroxybenzylidenehydantoin*, $C_{10}H_7O_5N_3$, which crystallised in rosettes of needles, m. p. 286°. The latter compound was reduced by means of tin and hydrochloric acid to the *hydrochloride* of *4-m'-amino-o-hydroxybenzylhydantoin*, $CO<^{NH\cdot CO}_{NH\cdot CH\cdot CH_2\cdot C_6H_3(OH)\cdot NH_2,HCl}$, decomp. 242—243°, and this was converted, through the diazo-reaction, into *4-om'-dihydroxybenzylhydantoin*, $C_{10}H_{10}O_4N_2$, a red powder with no definite m. p. This compound dissolves in alkalis and gives purple solutions in hydrochloric and sulphuric acids, but it is so unstable in these solutions that it could not be hydrolysed.

The above 5-nitro-2-hydroxybenzylidenehydantoin was methylated by methyl iodide and sodium methoxide to *4-m'-nitro-o-meth-*

oxybenzylidene-1-methylhydantoin, $CO<^{NMe\cdot CO}_{NH-C:CH\cdot C_6H_3(OMe)\cdot NO_2}$, m. p. 265°, and this was reduced as above to the *hydrochloride* of 4-m'-*amino*-o-*methoxybenzyl*-1-*methylhydantoin*. J. C. W.

Nitrated Proteins. I. Determination of the Structure of Nitrotyrosine. TREAT B. JOHNSON and EDWARD F. KOHMANN (*J. Amer. Chem. Soc.*, 1915, **37**, 1863—1884).—A study of the nitrated proteins is being undertaken, especially in connexion with their products of hydrolysis and the xanthoproteic and Millon's reactions. A short and useful review of the contributions to this subject since 1771 is given at the outset, and the earlier papers in this series will deal with the nitration of the amino-acids which contain benzene nuclei.

The first references to the action of nitric acid on tyrosine are those of Warren de la Rue (1848), Strecker (1850), and Städeler (1860), but until the appearance of a paper by Funk (T., 1912, **101**, 1004), it was always assumed that the "nitrotyrosine" obtained by the action of dilute nitric acid was an individual substance. Funk assumed that the product was a mixture of 2- and 3-nitrotyrosines, the former predominating. Evidence is now brought forward which shows conclusively that the proportions of these isomerides are just the reverse; 3-nitrotyrosine is the chief product, and 2-nitrotyrosine is formed in only very small amount.

Tyrosine was obtained from silk "noils," a waste product of the combing of silk which consists of nearly pure fibroin. For the nitration, 16 grams of tyrosine were suspended in 85 c.c. of water, and 43 c.c. of nitric acid (D 1·42) were slowly added, the mixture being kept in ice. After a few hours, the nitrate of nitrotyrosine separated, and this was carefully treated with dilute ammonia. The crude nitrotyrosine was then gently boiled with methyl iodide and methyl-alcoholic potassium hydroxide for several hours, when two quaternary salts were formed, which were separated by fractional crystallisation from alcohol. The chief of these, the *trimethylammonium iodide* of 3-*nitrotyrosine*, $OH\cdot C_6H_3(NO_2)\cdot CH_2\cdot CH(CO_2H)\cdot NMe_3I$, formed radiating clusters of yellow prisms, with $2H_2O$, m. p. 119°, whilst the more soluble *salt*, clusters of stout prisms, m. p. 220—221° (decomp.), agreed with the formula

$$OH\cdot \underset{NO_2}{C_6H_3}\cdot CH_2\cdot CH(NMe_3I)\cdot CO\cdot O\cdot NMe_3\cdot CH(CO_2H)\cdot CH_2\cdot \underset{NO_2}{C_6H_3}\cdot OH.$$

The protection afforded by the nitro-group to the hydroxyl group is evident, for tyrosine itself gives the quaternary salt of a methoxy-compound on methylation. Both of these quaternary salts lost trimethylamine when boiled with 10% sodium hydroxide, forming 3-nitro-4-hydroxycinnamic acid (this vol., i, 79), the yield being excellent. No isomeric acid could be discovered, and, therefore, it is proved that the chief product of the nitration of tyrosine is 3-nitrotyrosine.

3-Nitro-4-hydroxycinnamic acid was reduced by tin and hydrochloric acid to the *hydrochloride* of 3-*amino*-4-*hydroxycinnamic acid*,

$$CO_2H\cdot CH:CH\cdot C_6H_3(OH)\cdot NH_2,HCl,$$

decomp. 240°.

The condensation of the crude nitrotyrosine with ammonium thiocyanate and acetic anhydride led to different products which varied with the conditions. One experiment is described in which (*a*) a small amount of 2-*thio*-1 : 3-*diacetyl*-4-m-*nitro*-p-*acetoxybenzylhydantoin*,

$$CS\begin{cases}NAc\cdot CO\\ |\\ NAc\cdot CH\cdot CH_2\cdot C_6H_3(NO_2)\cdot OAc'\end{cases}$$

yellow needles, with $1MeCO_2H$, m. p. 174°, very sparingly soluble in glacial acetic acid, (*b*) more of 2-*thio*-3-*acetyl*-4-m-*nitro*-p-*acetoxybenzylhydantoin*, $C_{14}H_{13}O_6N_3S$, yellow, rectangular plates, m. p. 173—175°, readily soluble in glacial acetic acid, and (*c*) also 2-*thio*-4-o-*nitro*-p-*hydroxybenzylhydantoin*, $C_{10}H_9O_4N_3S$, which is soluble in water, were isolated. The latter compound, which proves the existence of 2-nitrotyrosine in the crude nitration product, crystallised from glacial acetic acid in rosettes of yellow needles with $1CH_3\cdot CO_2H$, and stout, red prisms, without acid of crystallisation, both forms decomposing at above 274°. Another experiment is described in which no tri- or di-acetyl derivatives were obtained, but 2-*thio*-3-*acetyl*-4-m-*nitro*-p-*hydroxybenzylhydantoin*,

$$CS\begin{cases}NH\text{--}CO\\ |\\ NAc\cdot CH\cdot CH_2\cdot C_6H_3(NO_2)\cdot OH'\end{cases}$$

clusters of flat prisms, m. p. 176—178°, and the above *o*-nitro-compound were identified as the products. The various acetyl derivatives were all hydrolysed by concentrated hydrochloric acid to 2-*thio*-4-m-*nitro*-p-*hydroxybenzylhydantoin*, $C_{10}H_9O_4N_3S$, hexagonal plates, m. p. 239—242° (decomp.), and this was desulphurised to 4-m-*nitro*-p-*hydroxybenzylhydantoin*, $CO\begin{cases}NH\cdot CO\\ |\\ NH\cdot CH\cdot CH_2\cdot C_6H_3(NO_2)\cdot OH'\end{cases}$ yellow needles, m. p. 225—226°.

2-Thio-3-benzoylhydantoin (A., 1912, i, 53) was condensed with 3-nitroanisaldehyde in the presence of acetic acid and anhydrous sodium acetate to form 2-*thio*-4-m-*nitro*-p-*methoxybenzylidenehydantoin*, $C_{11}H_9O_4N_3S$, decomp. 255°, which was desulphurised to 4-*m*-nitro-*p*-methoxybenzylidenehydantoin (Johnson and Bengis, A., 1912, i, 808). The benzyl compound corresponding with the latter (*ibid.*) gave the above 4-*m*-nitro-*p*-hydroxybenzylhydantoin on demethylation with acetic acid and hydrogen bromide. Both of these benzyl compounds could be reduced by red phosphorus and hydriodic acid to 4-*m*-amino-*p*-hydroxybenzylhydantoin (*ibid.*).

The above relationships are evidence of the correctness of the structure assigned to 3-nitrotyrosine. Another line of argument is as follows. 2-Thiohydantoin was condensed with anisaldehyde to 2-thio-4-anisylidenehydantoin (Johnson and O'Brien, A., 1912, i, 806), and reduced to 2-*thio*-4-*anisylhydantoin*, $CS\begin{cases}NH\cdot CO\\ |\\ NH\cdot CH\cdot CH_2\cdot C_6H_4\cdot OMe'\end{cases}$ plates, m. p. 215°, by means of sodium amalgam. This was desulphurised, or the anisylidene compound was desulphurised and then reduced, and by either means 4-anisylhydantoin (A., 1912, i, 808) was obtained. The product of the nitration (*ibid.*) and subsequent demethylation of this is the above 4-*m*-nitro-*p*-hydroxybenzylhydantoin.

The last-named compound, that is, the hydantoin of 3-nitrotyrosine, was also treated with methyl iodide and methyl-alcoholic potassium

hydroxide. With one molecular proportion of methyl iodide, the product was 1-*methyl*-4-m-*nitro*-p-*hydroxybenzylhydantoin*, $C_{11}H_{11}O_5N_3$, m. p. 202°, and with an excess, 1 : 3-*dimethyl*-4-m-*nitro*-p-*hydroxybenzylhydantoin*, m. p. 180—185°, was formed, but the protection afforded by the nitro-group prevented complete methylation. J. C. W.

Use of Cyanic Acid in Glacial Acetic Acid Solution and in Mixtures of Glacial Acetic Acid with other Organic Solvents. Derivatives of 3-α-Carboxy-α-methylethylamino-4-dimethylhydantoin. J. R. Bailey and W. T. Read (*J. Amer. Chem. Soc.*, 1915, **37**, 1884—1893).—Glacial acetic acid, alone or diluted with an inert solvent, is an excellent medium for the application of cyanic acid in condensations with primary or secondary amines, and is especially adapted to those cases in which the reaction will hardly take place under the usual conditions. Such a case is now described.

Ethyl hydrazodi*iso*butyrate, $N_2H_2(CMe_2\cdot CO_2Et)_2$ (Thiele and Heuser, A., 1896, i, 341), was dissolved in glacial acetic acid, and then solid potassium cyanate was gradually added, at below 40°. After warming the mixture at 60° for a time, it was diluted and neutralised by ammonia. The bulk of the product separated on cooling. An 86% yield of 3-α-*carbethoxy*-α-*methylethylamino*-4-*dimethylhydantoin*,

$$CO_2Et\cdot CMe_2\cdot NH\cdot N<\begin{matrix}CMe_2\cdot CO\\ |\\ CO\text{---}NH\end{matrix}>,$$

was thus obtained, in plates, m. p. 104—105°. A condensation of cyanic acid with free hydrazodi*iso*butyric acid or its nitrile could not be effected. The above compound was very readily oxidised by bromine water to a non-volatile *oil*, $C_{22}H_{36}O_8N_6$, which gave a sublimate of, probably, acetonylcarbamide, when heated at 110° in a vacuum.

The constitution of the condensation product was proved by the following series of changes. With sodium nitrite and glacial acetic acid, it formed the *nitroso*-compound,

$$CO_2Et\cdot CMe_2\cdot N(NO)\cdot N<\begin{matrix}CMe_2\cdot CO\\ |\\ CO\text{---}NH\end{matrix}>,$$

pale yellow laminæ, m. p. 104°, which was hydrolysed by concentrated potassium hydroxide to 3-α-*carboxy*-α-*methylethylnitrosoamino*-4-*dimethylhydantoin*, minute, rhombic plates, m. p. 165° (decomp.). The original ester was hydrolysed by concentrated potassium hydroxide to 3-α-*carboxy*-α-*methylethylamino*-4-*dimethylhydantoin*,

$$CO_2H\cdot CMe_2\cdot NH\cdot N<\begin{matrix}CMe_2\cdot CO\\ |\\ CO\text{---}NH\end{matrix}>,$$

long, slender, prismatic plates, m. p. 192·5°, and by 50% sulphuric acid at 110° to 3-*amino*-4-*dimethylhydantoin*, $NH_2\cdot N<\begin{matrix}CMe_2\cdot CO\\ |\\ CO\text{---}NH\end{matrix}>$. The latter compound was isolated by pouring the acid solution into cold ammonium hydroxide, evaporating to dryness and extracting with ethyl acetate, and was obtained in long, slender prisms, m. p. 170°. It is a powerful reducing agent, and forms a *benzoyl* derivative, $C_{12}H_{13}O_3N_3$, m. p. 241°, and a *benzylidene* compound, $CHPh{:}N\cdot N<\begin{matrix}CMe_2\cdot CO\\ |\\ CO\text{---}NH\end{matrix}>$, m. p

191—192°. This hydrazone was also prepared by the condensation of cyanic acid, in the above manner, with benzylidenehydrazino*iso*butyric acid, $CHPh{:}N{\cdot}NH{\cdot}CMe_2{\cdot}CO_2H$ (*loc. cit.*), a new preparation of which is described.

It was hoped that the 3-amino-4-dimethylhydantoin could be synthesised by the action of potassium cyanate on a solution of the hydrochloride of ethyl hydrazino*iso*butyrate (*loc. cit.*), but, in this case, the product was ethyl semicarbazino*iso*butyrate,

$$NH_2{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CMe_2{\cdot}CO_2Et$$

(A., 1903, i, 130). J. C. W.

Acetyl Derivatives of the Diphenylthiosemicarbazides. James Lyttle McKee (T., 1915, **107**, 1133—1144).—Thiocarbamide and many of its derivatives containing hydrocarbon radicles react additively with acyl haloids (Dixon and Taylor, T., 1912, **101**, 2502). The same is now shown to be true of *ac*-diphenylthiosemicarbazide, $\overset{a}{N}HPh{\cdot}\overset{b}{C}S{\cdot}\overset{c}{N}H{\cdot}NHPh$. When a suspension of this in benzene is treated with acetyl chloride, a *substance*,

$$NHPh{\cdot}NH{\cdot}C(NHPh){:}SAcCl,$$

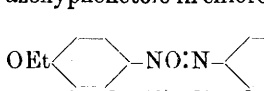
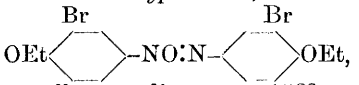
colourless crystals, m. p. 233° (decomp.), colouring at 160° and sintering at 218°, is obtained, which behaves like the salt of a moderately strong base; the *nitrate*, m. p. 173—174° (decomp.), and *picrate*, yellow crystals, m. p. 175°, have been prepared. When treated with an equivalent of cold, very dilute sodium carbonate solution or when heated with water on the steam-bath, the chloride loses hydrogen chloride and yields, by intramolecular rearrangement, *c-acetyl-ac-diphenylthiosemicarbazide*, $NHPh{\cdot}CS{\cdot}NH{\cdot}NAcPh$. This substance, the constitution of which is proved by its formation from phenylthiocarbimide and *as*-acetylphenylhydrazine, melts with effervescence at 160°, resolidifies, and then melts at 261°, having been converted by loss of water into an *anhydride*, $C_{15}H_{13}N_3S$, m. p. 265°, which can also be obtained from the original additive compound by heating it at its m. p. or by boiling it for some time with water, or by treating it with moderately concentrated alkali, and is most conveniently prepared by heating *ac*-diphenylthiosemicarbazide with acetic anhydride. A second product in the last reaction is a substance, m. p. 133°, to which Vahle in 1894 ascribed the constitution $NHPh{\cdot}CS{\cdot}NPh{\cdot}NHAc$. This constitution has now been confirmed, since the same substance has been obtained (1) by heating the additive compound of *ac*-diphenylthiosemicarbazide and acetyl chloride with an excess of alcoholic potassium hydroxide, (2) by treating a suspension of *ab*-diphenylthiosemicarbazide in benzene with acetyl chloride, and (3) by heating *ab*-diphenylthiosemicarbazide with acetic anhydride.

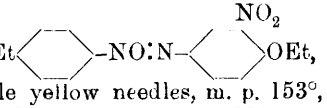
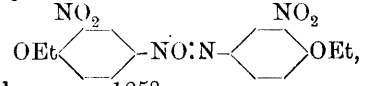
The *substance*, prismatic crystals, m. p. 161—162°, obtained by treating *ab*-diphenylthiosemicarbazide, suspended in acetone, with acetyl chloride and pouring the product into dilute alkali, is most probably *a-acetyl-ac-diphenylthiosemicarbazide*, $NAcPh{\cdot}CS{\cdot}NH{\cdot}NHPh$, since it yields acetic acid, phenylthiocarbimide, and phenylhydrazine by boiling with hydrochloric acid.

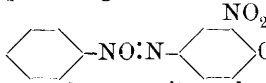
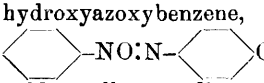
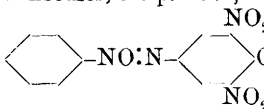
The *substance*, colourless crystals, m. p. 272·5°, obtained by the

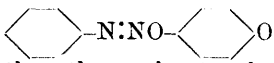
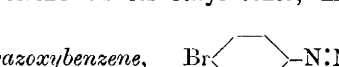
reaction between hydrazobenzene and acetylthiocarbimide in hot benzene, yields thiocyanic acid after being heated and boiled with water, and is therefore probably a-*acetyl*-bc-*diphenylthiosemicarbazide*, NHAc·CS·NPh·NHPh. C. S.

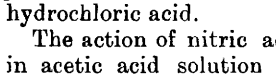
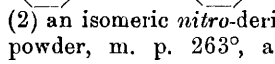
Electrical Conductivity of Tetrazole and its Derivatives at Various Temperatures. E. Oliveri-Mandalà (*Gazzetta*, 1915, **45**, i, 303—306).—The author has made further measurements of the electrical conductivity of tetrazole (A., 1914, i, 1144), and has extended his investigations to ethyl tetrazolecarboxylate, the ionisation of which also increases with rise of temperature. T. H. P.

New Derivatives of Azoxybenzene. Bruno Valori (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 284—292).—The action of bromine on azoxyphenetole in chloroform solution yields: (1) m-*bromoazoxyphenetole*,  , which crystallises in yellow needles, m. p. 126°; (2) *di*-m-*bromoazoxyphenetole*,  , which forms slender, yellow needles, m. p. 153°, and, like the preceding compound, gives *m*-bromo-*p*-phenetidine on reduction; (3) an isomeric *dibromoazoxyphenetole*, which forms a pale yellow, crystalline powder, m. p. 165°, and is obtained in very small proportion.

The action of nitric acid on azoxyphenetole in acetic acid solution yields: (1) m-*nitroazoxyphenetole*,  , which crystallises in a felted mass of pale yellow needles, m. p. 153°, and (2) *di*-m-*nitroazoxyphenetole*,  , which forms a yellow, crystalline powder, m. p. 185°.

The action of nitric acid on the ethyl ether of *a*-*p*-hydroxyazoxybenzene, m. p. 72° (compare Angeli, A., 1914, i, 882), yields m-*nitro*-*a*-p-*ethoxyazoxybenzene*,  , which forms yellow needles, m. p. 128°, and gives *m*-nitro-*p*-hydroxyazobenzene when treated with concentrated sulphuric acid. The corresponding *a*-*p*-hydroxyazoxybenzene, m. p. 156°, has, therefore, the structure  , and its *dinitro*-derivative, obtained in golden-yellow needles, m. p. 197°, is probably represented by the configuration  . The isomeric *β*-*p*-hydroxyazoxybenzene, m. p. 117° (Angeli, *loc. cit.*, gives 107°), should be

 , and this structure is confirmed by the fact that the action of bromine on its ethyl ether, m. p. 75°, gives mp′-*dibromo*-β-p-*hydroxyazoxybenzene*,  , which forms an amorphous, colourless powder, m. p. 135°, and yields *p*-bromoaniline and *m*-bromo-*p*-phenetidine on reduction with tin and hydrochloric acid.

The action of nitric acid on β-*p*-hydroxyazoxybenzene (m. p. 117°) in acetic acid solution yields: (1) m-*nitro*-β-p-*hydroxyazoxybenzene*,  , which forms minute needles, m. p. 171°; (2) an isomeric *nitro*-derivative, $C_{12}H_9O_4N_3$, obtained as a crystalline powder, m. p. 263°, and (3) mp′-*dinitro*-β-p-*hydroxyazoxybenzene*,  , m. p. 185°. T. H. P.

Oxidation of Azoketones and Azonitriles. A. Angeli (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 1185—1190).—*Benzeneazo*-p-*acetophenone*, NPh:N·C_6H_4·COMe, prepared by condensation of nitrosobenzene (1 mol.) and *p*-aminoacetophenone in acetic acid, forms shining, red laminæ, m. p. 115°, and gives an *oxime*, $C_{14}H_{13}ON_3$, m. p. 169°. When oxidised in acetic acid solution by means of hydrogen peroxide, it yields the two isomeric *benzeneazoxy*-p-*acetophenones*: (1) NPh:NO·C_6H_4·COMe, m. p. 132°, which forms an *oxime*, $C_{14}H_{13}O_2N_3$, m. p. 181°, and (2) O:NPh:N·C_6H_4·COMe, m. p. 92°. When oxidised by means of alkaline permanganate, the former of these azoxy-ketones yields β-azoxybenzenecarboxylic acid (compare Angeli and Valori, A., 1913, i, 533), whilst both yield the red p-*hydroxybenzeneazo*-p-*acetophenone*, OH·C_6H_4·N:N·C_6H_4·COMe, m. p. 134°.

Benzeneazo-p-*benzophenone*, NPh:N·C_6H_4·COPh, m. p. 106°, similarly obtained from nitrosobenzene and *p*-aminobenzophenone, is oxidised by hydrogen peroxide to an *azoxy*-compound, $C_{19}H_{14}O_2N_2$, m. p. 72°, which was not investigated owing to the small quantity available.

Benzeneazo-p-*phenylacetonitrile*, NPh:N·C_6H_4·CH_2·CN, similarly obtained from nitrosobenzene and *p*-aminophenylacetonitrile, forms orange-red laminæ, m. p. 127°, and, when treated with hydrogen peroxide, yields the isomeric *benzeneazoxy*-p-*phenylacetonitriles*: (1) O:NPh:N·C_6H_4·CH_2·CN, m. p. 94°, and (2) NPh:NO·C_6H_4·CH_2·CN, m. p. 132°; the latter compound yields β-azoxybenzenecarboxylic acid when oxidised by means of permanganate. T. H. P.

So-called Benzeneazoanthranol and its Methyl Ether. G. Charrier (*Atti R. Accad. Sci. Torino*, 1914—1915, **50**, 589—604; *Gazzetta*, 1915, **45**, i, 502—516).—The ethers of hydroxyazo-compounds are re-

garded as *O*-ethers, whereas to the corresponding hydroxyazo-compounds themselves some ascribe the enolic formulæ and others the ketonic formulæ of quinonehydrazones.

The author discusses more particularly the case of benzeneazoanthranol (compare Meyer and Zahn, A., 1913, i, 536), which he regards as anthraquinonephenylhydrazone, the enolic azoic formula being assigned only to its *O*-benzoyl derivative. The reasons advanced are briefly as follows: The absence of marked basic properties in this compound and in its methyl ether; the facility with which these compounds yield anthraquinone, even at the ordinary temperature; the fact that certain so-called enolic reactions, such as that with bromine water, are given by arylhydrazines and probably also by hydrazones, so that in the present case they cannot be attributed to the presence of the enolic grouping; and the complete failure of the diazo-scission characteristic of azo-compounds.

Treatment of anthraquinonephenylhydrazone (compare Kaufler and Suchannek, A., 1907, i, 225) with nitric acid (D 1·48) in ethereal solution yields anthraquinone and phenylhydrazine, the latter then undergoing more or less complete oxidation to benzenediazonium nitrate according to the conditions; this reaction yields also a small proportion of an unstable base, which reduces Fehling's solution with evolution of nitrogen and becomes intensely coloured in the air. Similarly, the methyl ether of anthraquinonephenylmethylhydrazone, when treated with nitric acid (D 1·48) in ethereal solution, yields anthraquinone and *as*-phenylmethylhydrazine, together with a small proportion of an auto-oxidisable base, probably analogous to that obtained from anthraquinonephenylhydrazone; no trace of benzenediazonium nitrate is formed, such an oxidation of phenylmethylhydrazine necessitating the preliminary elimination of the methyl group, which adheres strongly to the nitrogen atom.

If the methyl ether is treated with nitric acid dissolved in excess of ether and the mixture is kept cold, a *compound*, $C_{21}H_{15}O_3N_3$, separates, which forms orange-red leaflets with a golden reflexion, m. p. 240—241° (decomp.), and is probably a mononitro-derivative of the methyl ether. It dissolves in concentrated sulphuric acid giving a reddish-brown solution, from which it is reprecipitated unchanged on dilution. On prolonged boiling with concentrated hydrochloric acid and a little alcohol, it is hydrolysed completely into anthraquinone and a *base*, $C_7H_9O_2N_3$, which crystallises in transparent, yellow, prismatic needles, m. p. 142°, becoming opaque after a few hours, reduces Fehling's solution and ammoniacal silver nitrate solution in the cold, and is probably *as*-*p*-nitrophenylmethylhydrazine,

$$NH_2\cdot NMe\cdot C_6H_4\cdot NO_2.$$

The formation of the latter, together with anthraquinone, indicates the constitution, $O{:}C_{14}H_8{:}N\cdot NMe\cdot C_6H_4\cdot NO_2$, for the compound, m. p. 240—241°. The formation of such a compound, containing the nitro-group in the aromatic nucleus, by the action of nitric acid on the methyl ether furnishes a further proof of the great resistance generally exhibited by the quinonic grouping towards nitric acid compared with that of the aromatic nucleus. T. H. P.

Transformation of Arylhydrazine Nitrates, $NHAr\cdot NH_2.HNO_3$, into Aryldiazonium Nitrates, $NO_3\cdot NAr{:}N$, by the Action of Nitric Acid. G. CHARRIER (*Atti R. Accad. Sci. Torino*, 1914—1915, **50**, 779—793; *Gazzetta*, 1915, **45**, i, 516—528).—In studying the action of nitric acid in ethereal solution on anthraquinonephenylhydrazone, the author found that phenylhydrazine nitrate, obtained together with anthraquinone by a primary hydrolysis, undergoes more or less complete transformation into benzenediazonium nitrate (compare preceding abstract). The same change occurs when phenylhydrazine (1 mol.) and anthraquinone (1 mol.) are treated together with ethereal nitric acid; in absence of the quinone, small proportions of aryldiazonium nitrate are obtained, but in this case the reaction proceeds in a totally different manner.

The author has investigated the influence of anthraquinone on the reaction of nitric acid with other arylhydrazine nitrates and has also compared the activities of different quinones, in equimolecular proportions, in influencing the action of nitric acid on various arylhydrazine nitrates. The quinones employed were: *p*-benzoquinone, which oxidises phenylhydrazine with liberation of nitrogen and oxidises *as*-phenylalkylhydrazines into tetrazones, but reacts with *o*-nitro- and *op*-dinitro-phenylhydrazines with formation of *p*-hydroxyazo-compounds; thymoquinone or its polymeride, which yields arylhydrazones with arylhydrazines; β-naphthaquinone and phenanthraquinone, which form *o*-hydroxyazo-compounds; anthraquinone, which does not react with phenylhydrazine, but yields various arylhydrazones by indirect methods, and acenaphthenequinone, which reacts with arylhydrazines, forming arylhydrazones.

The results obtained confirm the conclusion that the transformation of arylhydrazine nitrates into aryldiazonium nitrates by the action of ethereal nitric acid proceeds in different ways according as quinones are present or absent. In the former case, the aryldiazonium nitrate is formed in large proportion, the quinone apparently impeding the action effected by the nitric acid in absence of quinone; only traces of nitrous vapours are evolved. In the latter case, the energetic reaction which takes place is accompanied by copious evolution of nitrogen and nitrous fumes, and can be readily explained as a simple oxidation of the arylhydrazine nitrate. The fact that nitric acid or its decomposition products are capable of oxidising arylhydrazine nitrates to aryldiazonium nitrates is not surprising in view of the transformation of arylhydrazines into diazonium salts effected, under certain conditions, by mercuric oxide or the halogens.

With some quinones, for instance, β-naphthaquinone and thymoquinone, the above reaction is almost quantitative and is found to take place by way of the nitrate of the corresponding hydroxyazo-compound; diazo-scission of the latter yields the diazonium nitrate, which is accompanied by the normal product of diazo-scission, namely, the corresponding nitrophenol. In the case of anthraquinone, which exerts a comparatively slight effect on the reaction, nitroanthranol is not found, but this could not be expected, since anthraquinonearylhydrazones are decomposed by nitric acid into anthraquinone and arylhydrazines, which, at temperatures somewhat above the ordinary, are

readily transformed in small amount into aryldiazonium nitrates. *p*-Benzoquinone, phenanthraquinone, and acenaphthenequinone do not hinder the conversion into aryldiazonium nitrates, which would take place by oxidation in their absence.

The properties of several new arylhydrazine nitrates which have been prepared show that, contrary to the usual statement, these compounds are in general highly stable, and may be fused unchanged in small quantities and recrystallised by cooling. In most cases, their decomposition by heat occurs slowly and with liberation of gas at temperatures a few degrees above the melting points. When heated slowly, they exhibit contraction in volume before, sometimes considerably before, they melt to colourless liquids. They are extremely soluble in water or 95% alcohol, and crystallise well from absolute alcohol; all contain 1 mol. of acid to 1 mol. of base.

Phenylhydrazine nitrate, m. p. 145—146°, melts without decomposition, and begins to turn yellow only at about 170° and to exhibit appreciable decomposition, with development of gas, at 185—190°.

o-*Tolylhydrazine nitrate* forms shining, white leaflets, contracting at about 75°, m. p. 98—100°.

m-*Tolylhydrazine nitrate* forms heavy, slender, acicular crystals, m. p. 145—147°, which begin to contract about 20° below their melting point.

p-*Tolylhydrazine nitrate* forms shining, white crystals, m. p. 152—153°, previously softening.

m-4-*Xylylhydrazine nitrate* forms shining, white laminæ, m. p. 146—147° (decomp.).

ψ Cumyl-5-*hydrazine nitrate* forms shining, colourless leaflets, m. p. 137—138° (decomp.).

o-*Anisylhydrazine nitrate* forms a voluminous, gelatinous mass, m. p. 108° (decomp.).

p-*Anisylhydrazine nitrate* forms colourless, prismatic, acicular crystals, m. p. 95—96° (decomp.), which are rapidly turned red and then violet by the action of light and air.

p-*Phenetylhydrazine nitrate* forms shining, white laminæ, contracting at 98—100°, and turning red in the light and air, m. p. 107—108° (decomp.). T. H. P.

Action of *p*-Nitroso-bases on Hydrazines. Otto Fischer and W. Johannes (*J. pr. Chem.*, 1915, [ii], **92**, 60—73).—By the interaction of phenylhydrazine and *as*-phenylmethylhydrazine with *p*-nitrosoaniline and its alkyl derivatives, Fischer and Wacker (A., 1888, 1286; 1889, 702; compare also Fischer and Hepp, A., 1888, 460) have described a number of condensation products, which they termed diazobenzenenitrosoanilines. It is now pointed out that these compounds are simply the *p*-amino-substitution products of the diazoxyaminobenzenes, obtained by Bamberger (A., 1898, i, 20; 1899, i, 589) by the condensation of diazonium salts with *β*-phenylhydroxylamine, and are best represented by one of the following formulæ:

$$NR_2\cdot C_6H_4\cdot NO{:}N\cdot NPhR' \text{ or } NR_2\cdot C_6H_4\cdot \overset{O}{\underset{\diagdown\!\diagup}{N}}\!\!-\!\!-\!\!-N\cdot NPh\cdot R'.$$

The authors prefer the second of these two formulæ, as they find that the product from *p*-nitrosodimethylaniline and *as*-phenylmethylhydrazine (R and R′ = Me) can be volatilised without undergoing decomposition, a behaviour which would not be expected if the compound contained a quinquevalent nitrogen atom, as shown in the first formula.

The new condensation products described below were all prepared by the interaction of the *p*-nitrosoaniline hydrochlorides and arylhydrazine acetates in aqueous or dilute acetic acid solution at 0°.

p-*Ethylaminobenzenediazoxyaminobenzene*, $NHEt\cdot C_6H_4\cdot N_2O\cdot NHPh$, from *p*-nitrosoethylaniline and phenylhydrazine, forms yellow prisms or leaflets, decomp. 122—123°, and is decomposed by boiling dilute mineral acids or alkalis, with evolution of nitrogen and the formation of various products, amongst which phenol and *p*-nitrosoethylaniline have been identified.

p-*Ethylaminobenzenediazoxymethylaminobenzene*,

$$NHEt\cdot C_6H_4\cdot N_2O\cdot NMePh,$$

prepared from *p*-nitrosoethylaniline and *as*-phenylmethylhydrazine, crystallises in canary-yellow needles, m. p. 97°.

p-*Methylaminobenzenediazoxymethylaminobenzene*, yellow prisms, m. p. 98—100°.

p-*Dimethylaminobenzenediazoxyphenylaminobenzene*,

$$NMe_2\cdot C_6H_4\cdot N_2O\cdot NPh_2,$$

from *p*-nitrosodimethylaniline and *as*-diphenylhydrazine, forms yellow needles or prisms, m. p. about 150° (decomp.). p-*Methylaminobenzenediazoxyphenylaminobenzene*, yellow needles, decomp. 167°. 4-p-*Dimethylaminobenzenediazoxyaminobromobenzene*, from *p*-bromophenylhydrazine and *p*-nitrosodimethylaniline, forms yellow needles or prisms, m. p. 128° (decomp.), and is decomposed by boiling dilute sulphuric acid into bromobenzene and *p*-aminodimethylaniline, with evolution of nitrogen.

p-Dimethylaminobenzenediazoxymethylaminobenzene yields a *picrate*, small, yellow prisms, *methiodide*, lustrous, yellow leaflets or clusters of needles, m. p. 147°, and on reduction with zinc dust and acetic acid at 0° is converted into methylaniline, *p*-aminodimethylaniline, and *as*-phenylmethylhydrazine. When boiled with dilute sulphuric acid, it yields, amongst other products, phenol and methylaniline.

The *picrates* of the diazoxyamino-compounds, $C_{14}H_{16}ON_4$ (microscopic, yellow prisms) and $C_{13}H_{14}ON_4$ from *p*-nitrosoaniline and *as*-phenylmethylhydrazine (*loc. cit.*), yellow needles, decomp. about 114°, are also described.

The *compound* from α-naphthylhydrazine and *p*-nitrosodimethylaniline spontaneously decomposes even at a low temperature with separation of naphthalene and evolution of nitrogen.

β-p-*Dimethylaminobenzenediazoxyaminonaphthalene*,

$$NMe_2\cdot C_6H_4\cdot N_2O\cdot NH\cdot C_{10}H_7,$$

from β-naphthylhydrazine and *p*-nitrosodimethylaniline, forms yellow needles.

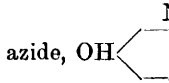
Semicarbazide reacts with *p*-nitrosodimethylaniline and *p*-nitroso-

aniline, yielding p-*dimethylaminobenzenediazoxycarbamide*, $NMe_2 \cdot C_6H_4 \cdot N_2O \cdot NH \cdot CO \cdot NH_2$, stellar aggregates of greenish-yellow needles, m. p. about 181°, and p-*aminobenzenediazoxycarbamide*, yellow needles, which begin to decompose above 220°. F. B.

Oxidation of Dimethylaminoazobenzene. A. Angeli (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 1190—1192).—Numerous investigations made by the author have shown that, when treated with hydrogen peroxide in acetic acid solution, compounds containing an azo-group take up only one oxygen atom, with formation of azoxy-compounds, O:NR:NR. A different course is taken by this reaction when the azo-compound contains a third tervalent nitrogen atom. When this atom is present in the form of an amino-group, the compound undergoes the usual transformations of aromatic amino-derivatives, and the hydroxylamine derivative, which is probably formed in the first phase, undergoes successive oxidation to nitroso- and nitro-compounds, and is partly transformed into substances containing new azo- and azoxy-groups. Much more simple is the case of a disubstituted amino-compound, with which the aminic nitrogen atom takes up an oxygen atom to form the corresponding oxide.

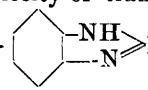
Thus *p*-dimethylaminoazobenzene is converted in this way into the *compound*, $NPh:NO \cdot C_6H_4 \cdot NMe_2:O$, which forms shining, golden laminæ, m. p. 127° (decomp.), and yields a *sulphate*, $(C_{14}H_{15}O_2N_3)_2,H_2SO_4$, m. p. 156° (decomp.). In aqueous solution, the base is reduced by hydrogen sulphide, giving *p*-dimethylaminoazobenzene, and also by hydroxylamine hydrochloride or hydrazine sulphate. When treated with bromine and subsequently reduced with tin and hydrochloric acid, it yields a base, which is converted into *p*-bromobenzanilide by benzoyl chloride. Since, under similar conditions, ordinary azoxy-compounds do not furnish salts, it must be assumed that the acid of the sulphate is united to the group $O:NMe_2$·; the salt is, therefore, probably an oxonium compound, $\begin{matrix} X \\ H \end{matrix}\!\!>\!O:NMe_2$· (compare Meisenheimer, A., 1913, i, 447). Since the nitrogen atom united to the two methyl groups and the oxygen atom is quinquevalent, structures for the base and its salts similar to those suggested by Hantzsch for the dimethylamino-azobenzenes and their salts are not possible and, indeed, the base and its salts are of the same colour.

Oxidation of the sodium salt of helianthin by similar means yields a *compound* which forms yellow crystals, m. p. 233° (decomp.), and is not reddened by acids; this compound was not investigated further. T. H. P.

Action of Azoimide on Quinone. E. Oliveri-Mandala and E. Calderaro (*Gazzetta*, 1915, **45**, i, 307—313).—In benzene solution, the action of azoimide on *p*-benzoquinone yields quinhydrone and the azide,  . The nitrogen-free compound described

by Escales (A., 1905, i, 145) is probably quinhydrone, and the fact that this author did not observe the formation of the azide is probably due to the low concentrations employed. The results now obtained indicate that hydrochloric acid and azoimide act similarly on quinone. The most satisfactory explanation of the reaction in the former case is that given by Schmidlin (A., 1911, i, 727), and on this basis it may be assumed that the interaction of azoimide and quinone proceeds in the following stages:

(1) $O{:}C_6H_4{:}O + N_3H \rightleftarrows OH{\cdot}C_6H_3N_3{\cdot}OH$;

(2) $OH{\cdot}C_6H_3N_3{\cdot}OH + O{:}C_6H_4{:}O \rightleftarrows O{:}C_6H_3N_3{:}O + OH{\cdot}C_6H_4{\cdot}OH$; (3) quinone + quinol = quinhydrone; (4) quinhydrone + azoimide = quinol + $OH{\cdot}C_6H_3N_3{\cdot}OH$, and (5) quinol + $O{:}C_6H_3N_3{:}O \rightleftarrows$ quinone + $OH{\cdot}C_6H_3N_3{\cdot}OH$. Owing to the ease with which the N_3-group undergoes isomerisation, the existence of the azide, $O{:}C_6H_3N_3{:}O$, is possible only on the assumption that the velocity of transformation into the triazole compound, $O{:}C_6H_3N_3{:}O \longrightarrow$  , is very small compared with that of the reaction $O{:}C_6H_3N_3{:}O \longrightarrow OH{\cdot}C_6H_3N_3{\cdot}OH$.

The action of a large excess of azoimide on quinone results in the precipitation of greenish-grey leaflets showing metallic lustre; after about fifteen minutes, these dissolve in the liquid with development of heat. The substance thus precipitated decomposes at about 100°, or, if slowly heated, at 130°, and has the composition of the additive compound, $C_6H_6,C_6H_4O_2,N_3H$. It has been shown by Meyer (A., 1908, i, 731) that, with acids and certain metallic chlorides, quinone forms unstable, highly coloured, additive compounds, some of which contain benzene of crystallisation.

Triazoquinol, $OH{\cdot}C_6H_3N_3{\cdot}OH$, forms nacreous leaflets, and assumes a red colour in the light. It is exceedingly stable towards shock, but explodes violently when heated. When heated with aqueous alcohol or treated with cold acid or alkali, it yields nitrogen and azoimide, and when shaken with a benzene solution of quinone it gives quinhydrone without evolution of nitrogen. It dissolves in ammonia solution, giving a green coloration which changes to red, nitrogen being liberated. T. H. P.

The Non-Acid and Non-Alkaline Hydration of Protein. MARTIN H. FISCHER and ANNE SYKES (*Kolloid. Zeitsch.*, 1915, **16**, 129—144).—The hydration (swelling) of colloids under the influence of acids and alkalis has been frequently investigated, but comparatively little is known with respect to the effects produced by substances of neutral character. These are presumably of great importance in the hydration of colloids (proteins) in the animal organism, and information on the subject has been sought by experiments in which the influence of carbamide, pyridine, and ethylamine on the hydration of gelatin was determined.

The hydration of gelatin in contact with water is increased by the addition of carbamide. If hydrochloric acid or sodium chloride is added to the carbamide solutions, the hydration increases, but decreases on the addition of dextrose.

The swelling of gelatin in water is also increased by the addition of pyridine, but this is partly due to the alkalinity of the solution, for on the addition of gradually increasing quantities of hydrochloric acid to a pyridine solution, the hydration is found to become smaller at first, but increases on the addition of larger quantities of acid. The swelling of gelatin in a pyridine solution is reduced by the addition of sodium chloride, but the dehydrating action of the salt decreases as the quantity of sodium chloride added is increased. Dextrose has also a dehydrating effect on the swelling of gelatin in pyridine solutions. In this case the effect increases with the concentration of the dextrose.

The effect of hydrochloric acid on the swelling of gelatin in solutions of ethylamine is similar to that observed with pyridine solution. Sodium chloride has a dehydrating effect which increases with the salt concentration, and dextrose behaves similarly. H. M. D.

Action of Chymosin [Rennet] and Pepsin. III. Different Susceptibility of Pepsin and Chymosin to Alkali. Olof Hammarsten (*Zeitsch. physiol. Chem.*, 1915, **94**, 291—323. Compare this vol., i, 726).—A new method is described for preparing from the gastric mucous membrane of young calves (one to two days old), a solution containing pepsin and chymosin with only traces of extraneous protein and other substances.

The acid extract of the gastric mucous membrane as ordinarily prepared is exactly neutralised with sodium hydroxide solution, using as indicator blue, red, and neutral litmus papers. After twenty-four hours, the liquid is centrifugated and the deposit, after careful washing, ground with water in a mortar. The turbid liquid is diluted with water to about the same volume as the original extract and filtered until clear. The bright, colourless filtrate may be preserved for a considerable time under toluene.

The solution thus obtained contains 0·012 to 0·040% of solid matter, and possesses peptic and chymotic powers. When it is treated with sodium hydroxide solution at room temperature, the pepsin is destroyed very much more quickly than the chymosin, so that after a short time a solution is obtained which contains only a slight amount of peptic power, although it still retains the power of rapidly clotting milk. This result confirms the view that pepsin and chymosin are separate enzymes. H. W. B.

Influence of Sodium Hydroxide on the Synthesising and Hydrolysing Properties of α-Glucosidase (Glucosidase of Bottom Yeast Dried in the Air). Em. Bourquelot and A. Aubry (*Compt. rend.*, 1915, **161**, 184—186. Compare this vol., i, 604).—The authors have studied the effect of adding increasing very small amounts of sodium hydroxide to solutions of dextrose in aqueous methyl alcohol containing α-glucosidase, the direct effect of the alkali on the sugar (compare Lobry de Bruyn, A., 1896, i, 116) being eliminated by a similar series of solutions from which the enzyme was omitted. The synthesising action is not appreciably affected so long as the medium remains faintly acid or even neutral to phenolphthalein, but as soon as this stage is passed, and alkalinity can be detected,

synthesis ceases, addition of further alkali producing isomerisation. Similarly, the same amount of alkali which stops synthesis also stops the hydrolysis of the methyl glucoside by the same enzyme. W. G.

Arginase : New Titrimetric Method for its Investigation. I. ANTONINO CLEMENTI (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 517—523. Compare this vol., i, 606).—The action of arginase on arginine may be followed by titration, in presence of formaldehyde, of the arginine solution with *N*/5-sodium hydroxide solution, before and after the action of the enzyme (compare Sörensen, A., 1908, i, 115). When titrated in this way, carbamide acts as a neutral compound, arginine sulphate as a monobasic acid, and ornithine sulphate as a dibasic acid. Consequently, when arginine is converted into carbamide and ornithine, the amount of alkali required for neutralisation is doubled.

Arginase is found to occur, not only in the pressed juice, but also in the aqueous extract of the livers of mammals. T. H. P.

Some Heterocyclic Organo-Silicon Compounds. ARTUR BYGDÉN (*Ber.*, 1915, **48**, 1236—1242).—The only cases described hitherto of compounds containing rings of which the constituent atoms are only carbon and silicon are rather indefinite substances prepared by the action of sodium on a mixture of silicon tetrachloride with trimethylene bromide or *o*-dichlorobenzene (Hart, *Brit. Ass. Rept.*, 1887, 661). By the action of the organo-magnesium compound derived from 1 : 5-dibromopentane on silicon tetrachloride in ethereal solution the author has obtained cyclo*pentamethylenesilicon dichloride*,

$$CH_2\langle\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\rangle SiCl_2,$$

as a clear pungent liquid, b. p. 169·5—170·5°/764 mm. (corr.), D_4^{20} 1·1560, $n_D^{20\cdot2}$ 1·46973, which is hydrolysed by water with formation of a yellowish-brown solid representing in all probability a *polymeride* of cyclo*pentamethylenesilicone*, $CH_2\langle\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\rangle SiO$.

If in the above synthesis, dimethylsilicon dichloride is taken in place of silicon tetrachloride, the product is *dimethyl*cyclo*pentamethylenesilicane*, $CH_2\langle\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\rangle SiMe_2$, a colourless, easily inflammable liquid of feeble camphor-like odour, b. p. 133—134°/752·9 mm. (corr.), D_4^{20} 0·8039, $n_D^{20\cdot1}$ 1·43940. An attempt to prepare *diethyl*cyclo*pentamethylenesilicane* in a similar manner gave only an impure product, b. p. 184—194°. D. F. T.

Physiological Chemistry.

Phagocytes and Respiratory Centre. H. J. HAMBURGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1325—1342).—Phagocytosis is accelerated by exposing phagocytes for half an hour to a medium from which oxygen has been almost entirely

removed. After five hours, retardation sets in. The respiratory centre behaves in an analogous manner; lack of oxygen causes increased respiration up to a certain point. There is a corresponding behaviour of the two species of cells when exposed to potassium cyanide, carbon dioxide, or anæsthetics (here lack of oxygen will explain the reaction). Increased sensitiveness as a result of partial oxygen withdrawal is probably a general phenomenon, and is further illustrated by the behaviour of the "vomiting centre." W. D. H.

The Hydrogen Ion Concentration of the Blood under Various Abnormal Conditions. M. L. MENTEN and G. W. CRILE (*Amer. J. Physiol.*, 1915, **38**, 225—232).—The hydrogen ion concentration of the blood during certain emotions, such as fright and anger, is increased up to pH = 7·00. This is probably due to increased carbon dioxide tension. In anæsthesia caused by ether, nitrous oxide, and chloroform, it may be increased to the same extent; the change in acidity begins when the anæsthetic begins to react with the blood, and depends on the degree of anæsthesia; restoration to normal is complete forty-five minutes after the administration ceases. In two cases of shock, the acidity of the blood was greatly increased. The blood flowing from the adrenal gland is always more alkaline than other venous blood; this is local, and is due to adrenaline. W. D. H.

Urinary and Blood Nitrogen in the Dog after Feeding. O. H. PERRY PIPER and J. HAROLD AUSTIN (*Proc. Soc. expt. Biol. Med., New York*, 1915, **12**, 179—181).—The non-protein nitrogen in the blood (Folin's method) reaches its maximum two hours after feeding, and returns to its original level in about ten to fourteen hours. On an excessive meat diet, the increase may be 25—40 mg. in six to eight hours, and even after twenty-four hours the original level is not reached. The curve follows closely that of urinary nitrogen. The total amount of urine varies independently. W. D. H.

The Sugar Content of the Blood of Cats under the Influence of Cocaine. EDWARD W. E. SCHEAR (*Amer. J. Physiol.*, 1915, **38**, 269—273).—Cocaine in itself causes no effect on the sugar of the blood. Hypoglycæmia when observed was due to excitement. W. D. H.

The Amino-acid Content of the Blood. PAUL GYÖRGY and EDGARD ZUNZ (*J. Biol. Chem.*, 1915, **21**, 511—537).—In dogs, the amino-acid content of the whole blood, and of plasma and corpuscles, is very constant; it is increased by hæmorrhage, but with simultaneous injection of Ringer's fluid it falls. It does not change on a protein-poor diet (potatoes), but rises markedly on a protein-rich diet (beef), especially in the corpuscles and in the arterial blood. W. D. H.

The Origin of Antithrombin. GEORGE P. DENNY and GEORGE R. MINOT (*Amer. J. Physiol.*, 1915, **38**, 233—247).—The work of previous observers, which showed that antithrombin is formed in the liver, is supported. Although normally no difference is found between hepatic and other venous blood, yet when stasis is produced, the liver alone shows a definite increase of antithrombin. Perfusion of the liver with defibrinated blood causes an increase of antithrombin in the perfusate, whereas perfusion of other parts shows no increase, or usually a decrease. Injection of small amounts of thrombin into the portal circulation caused a slight rise in antithrombin, but attempts to stimulate the liver to antithrombin formation by means of bile-salts, secretin, and electric stimulation failed. Dogs with phosphorus poisoning and liver destruction show a marked increase in antithrombin and a diminution of fibrinogen in their blood. W. D. H.

The Effect of Serum on Tissues. S. FELDSTEIN (*Proc. Soc. expt. Biol. Med., New York*, 1915, **12**, 187—191).—Instead of Abderhalden's complex dialysis method of examining enzymes in serum, a method is proposed, and has been used with good results, of noting the changes produced on the tissue in microscopic sections. W. D. H.

Enzyme of Saliva which Separates Hydrogen Sulphide from Horse-radish. M. H. P. P. VAN HAEFF (*Arch. Néerland*, 1915, [iii B], **2**, 377—384).—It was found that hydrogen sulphide is produced when horse-radish is mixed with saliva, and that more is produced in a mixture of a given weight of horse-radish and saliva, obtained by masticating, than with horse-radish finely ground with sand and mixed with saliva, indicating that the enzyme of saliva becomes adapted. The activity of the enzyme is increased by masticating horse-radish every day for a month. The enzyme, which is not identical with ptyalin, is not always present in saliva. Pure oil of mustard does not give the same action as horse-radish when mixed with saliva. N. H. J. M.

The Physiology of the Stomach. XXV. Normal Human Gastric Juice. A. J. CARLSON, H. HAGER, and M. P. ROGERS (*Amer. J. Physiol.*, 1915, **38**, 248—268).—The observations were mainly on the appetite juice obtained from two cases of gastric fistula. Details are given of the total solids, specific gravity, osmotic concentration, and total nitrogen. Most of the nitrogen is present as protein, a little as ammonia and amino-acids; the proteins, including mucin, undergo autodigestion when the juice is incubated at 38°. The protein is not toxic, although it acts as sensitiser to serum proteins. The acidity of the freshly secreted juice is 0·5% hydrochloric acid; the subsequent reduction which occurs is explained in the same way as Boldyreff (A., 1914, i, 617) explains it. Figures are also given for total chlorides, and experiments on the concentration of pepsin indicate that pepsin occurs in excess of the needs of the body. This large excess explains how it is that

reduction does not impair gastric digestion, and the uselessness of commercial pepsin clinically. W. D. H.

Acidity Curves in the Stomach and Duodenum. J. F. McClendon (*Amer. J. Physiol.*, 1915, **38**, 191—199).—Using the recently introduced methods of the author (see this vol., ii, 689), it is found that the acidity of an adult stomach rises rapidly during the first one and a-half to three hours after a meal, and then remains stationary until nearly all the food has left the stomach. The rise is slower with a heavy meal rich in protein. The height to which the acidity rises is a personal characteristic. The duodenal contents are slightly alkaline; the hydrogen ion concentration is about 0·00000002. The acidity of the infant's stomach (first month) rises slowly for fifteen minutes to one hour after nursing, and then rises rapidly until the stomach is empty, so that in four hours it may be as acid as in the adult; this activates pepsinogen, but as there is so little milk left in the stomach by this time, peptic digestion appears to be unimportant. The infant's duodenum is more acid than the average acidity of the stomach; pepsin is always present, and peptic digestion must take place there. W. D. H.

Metabolism of Amino-acids in the Organism. VI. Fate of Amino-acids Contained in the Lumen or Mucus of the Intestine. Ugo Lombroso and Camillo Artom (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 863—869. Compare this vol., i, 616, 857).—The amount of amino-acids in blood is invariably increased after circulation through an intestinal segment, and with blood containing no added amino-acid, the increase is almost always greater than the amount disappearing from the intestinal mucus. It may be that the enzymes of the mucus behave similarly to those of the pancreatic secretion, which is able to effect alternate hydrolysis and synthesis of fat according to the medium in which it acts and to its treatment (compare Lombroso, A., 1913, i, 664).

In cases where considerable proportions of amino-acids are introduced into the blood, their increase in the latter is always less than the diminution observed in the intestine. No sensible variation in the content of acetone compounds occurs, and the proportion of ammonia is always raised, but to a limited extent.

T. H. P.

Fat Absorption from the Stomach. Emil J. Baumann (*Proc. Soc. expt. Biol. Med., New York*, 1915, **12**, 183).—Histologically demonstrable fat enters the stomach walls by physicochemical processes, but in no case could any increase of fat in circulating fluids be shown. The conclusion drawn is that no true absorption of fat occurs in this organ. W. D. H.

Metabolism in the Dog before and after Splenectomy. Samuel Goldschmidt and R. M. Pearce (*Proc. Soc. expt. Biol. Med., New York*, 1915, **12**, 198).—The removal of the spleen in dogs produces no change in metabolism of nitrogen, fat, or iron.

W. D. H.

The Influence of the Composition and Amount of the Mineral Content of the Ration on Growth and Reproduction. E. V. McCollum and Marguerite Davis (*J. Biol. Chem.*, 1915, **21**, 615—643).—It has been generally assumed that excess of any mineral salt in diet is got rid of by excretory channels; it is, however, important to ascertain the effect of prolonged administration of unsatisfactory mineral mixtures, as it is well known that unbalanced salt solutions profoundly affect egg-cells. The present experiments on rats (illustrated by tables and charts) form a preliminary attempt to throw light on the subject. It was found that, provided other factors in the ration are adequate, growth and health are normal even although the mineral portion varies widely in amount, and even if it is highly acid. This, however, is not sufficient evidence that the ration is really adequate; it is only physiologically sufficient if normal reproduction and rearing of young at the normal intervals takes place also. An addition of salts to correct the mineral content of wheat fulfilled these conditions when butter-fat was given also. The work is in progress, and judgment on many points is for the present withheld.

W. D. H.

The Preservation of the Life of the Frog's Egg, and the Initiation of Development by Increase in Permeability. J. F. McClendon (*Amer. J. Physiol.*, 1915, **38**, 163—172).—Fertilisation or electric stimulation increases the permeability of the frog's egg so that sodium, potassium, lithium, magnesium, calcium, chlorine, SO_4 and CO_3 ions diffuse out at a faster rate; probably the swelling of the "pericardium of the egg" due to pure salt solution is caused by too great increase in permeability. In spite of the outward diffusion of salts, the egg absorbs water, and if this is prevented by the addition of osmotic substances, segmentation and gastrulation do not occur. The rapid swelling of the unfertilised egg is probably the cause of its death; the increase in permeability on fertilisation lowers the osmotic pressure and saves its life.

W. D. H.

The Perfusion of the Mammalian Medulla; the Effect of Calcium and Potassium on the Respiratory and Cardiac Centres. D. R. Hooker (*Amer. J. Physiol.*, 1915, **38**, 200—208).—The medulla of the dog may be successfully perfused with a saline solution in which dog's blood corpuscles are suspended. The cardiac and respiratory centres continue to act for upwards of two hours. The perfusing fluid must be properly aërated; an apparatus for this purpose is described. If calcium predominates over potassium, the respiratory centre is stimulated, and the heart's rate increased; if potassium predominates, the reverse occurs. When the accelerator nerves are cut, increase of potassium causes cardiac slowing, and increase of calcium slight cardiac acceleration. When the vagi are cut, increase of calcium causes definite cardiac acceleration, whereas increase of potassium produces slight cardiac slowing.

W. D. H.

Metabolism of Amino-acids in the Organism. VIII. Action of Hepatic Tissue on Amino-acids Added to Circulating Ringer's Solution. Ugo Lombroso and Corrado Luchetti (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 1253—1258).—When Ringer's liquid containing an amino-acid is circulated through isolated dog's liver, a diminution occurs in the content of the amino-acid in the liquid depending on its character, being greatest for asparagine and least for leucine; glycine and alanine occupy intermediate positions. In the case of leucine, the loss in the solution is more than counterbalanced by the increased amount of amino-acids in the hepatic tissue, whilst with asparagine such increase is small. In all instances, the amount of ammonia in the liquid and tissue after the circulation is moderately high, the deficit of amino-acid being largely, although not completely, accounted for in this way. When Ringer's solution, without amino-acid, is circulated through isolated dog's liver, a certain quantity of amino-acid passes from the tissue into the liquid; in one experiment, the amount of amino-acid in the tissue diminished, and in another, in which the circulating liquid contained dextrose, it showed marked increase. In all the experiments, whether amino-acids were added or not, and whether the animal was previously fed or kept for a long time without food, the proportion of ketogenic substances in the hepatic tissue diminished considerably; such diminution was not accounted for by passage of these substances into the circulating liquid, which invariably contained only small amounts of them. The conclusion is therefore drawn that, even without the co-operation of the oxidising action of the blood, hepatic tissue is capable of consuming ketogenic substances. T. H. P.

The Function of the Liver in Formation of Urea from Amino-acids. B. C. P. Jansen (*J. Biol. Chem.*, 1915, **21**, 557—561).—Contrary to the opinion of Folin and to the perfusion experiments of Fiske and Karsner, it is shown that if the arterialisation of the blood is properly maintained in perfusion experiments, the liver plays an important part in the production of urea from the amino-acids glycine, leucine, and alanine. W. D. H.

Recognition of Histidine by Colour Reactions. Hermann Pauly (*Zeitsch. physiol. Chem.*, 1915, **94**, 427—428. Compare Aldrich, this vol., i, 99).—Polemical. The author maintains that since the diazo-reaction is twenty to fifty times as delicate as any other colour reaction for histidine, the positive outfall of the diazo-reaction indicating the presence of histidine in the pituitary lobe should not be disregarded because of the negative results afforded by other histidine colour reactions. H. W. B.

Chemical and Chemico-physical Properties of Muscles and Muscular Juices. V. Content of Water, Total Nitrogen, and Extractive Nitrogen in White and Red Striped Muscle. G. Quagliariello (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 634—638. Compare this vol., i, 479).—In birds, the solid residue of white muscle is constantly and sensibly greater than that of red; with

the rabbit, the two are almost equal. The total nitrogen content of white muscle is invariably greater than that of red muscle with both birds and the rabbit, the difference being the greater in the latter case; the extractive nitrogen is also the more abundant in white than in red muscle. T. H. P.

Metabolism of Amino-acids in the Organism. V. Metabolism of Amino-acids Circulating in Functioning Muscle. Ugo Lombroso and Ludovici Paterni (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 870—876. Compare this vol., i, 616, 857).—The diminution in the amount of amino-acid dissolved in blood circulating in active muscular tissue is markedly greater than that occurring under similar conditions in resting muscle. The accumulation of amino-acids in muscular tissue, which is the principal cause of the disappearance of the amino-acids from the blood in resting muscle, is not exhibited with functioning muscle; with the latter, the content of amino-acids pre-existing in the tissue sometimes even diminishes. When blood alone is circulated through active muscle, the total amino-acids in the blood and muscular tissue often decrease. The amount of ammonia in the blood after circulation varies considerably in different experiments, and bears no relation to the extent to which the amino-acids disappear. Still more variable results are obtained with reference to the formation of acetone substances. Contrary to the statements of Embden and his collaborators (A., 1906, ii, 375; 1908, ii, 515), muscular tissue is capable of forming acetone substances in marked quantities, and alanine, far from exerting an inhibiting influence on the production of acetone, may actually be the origin of it. T. H. P.

Arginase. II. Its Distribution in the Organism and among the Vertebrates. Antonino Clementi (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 612—616).—The results of the investigation of arginase by the author's titrimetric method (this vol., i, 912) are in accord with those obtained by Kossel and Dakin's method of precipitation with silver nitrate.

Arginase is present in the liver of mammals, amphibia, and fishes, but not in that of birds or, in general, reptiles. It is contained in the kidneys of mammals, but, whilst hepatic arginase is found both in the aqueous extracts and in the pressed juice, that of the kidneys of mammals cannot be obtained by simple aqueous extraction. The enzyme is absent from aqueous extracts of the spleen, intestinal mucus, and muscles of mammals, birds, amphibia, reptiles, and fishes.

Attention is drawn to the following two points: (1) The lack of arginase in the liver of those vertebrates with which the liver elaborates uric acid in place of carbamide, namely, birds and reptiles, and its occurrence in the liver of all other vertebrates with which carbamide is secreted. (2) The presence of arginase in the kidneys of mammals, and the impossibility of obtaining it by simple aqueous extraction of renal tissue from other vertebrates, with the sole exception of birds.

A biological demonstration is thus furnished of the participation of arginase in the liver of mammals (amphibia and fishes) in the elaboration of carbamide. Further, the presence of the enzyme in the kidneys, and its absence from the liver, of birds, throw light on the physiological determination of the formation of ornithuric acid, which, with these vertebrates, occupies the place of hippuric acid among the catabolic products of the urine. T. H. P.

Metabolism of Creatine and Creatinine. X. The Relationship Between Creatine and Creatinine in Autolysing Tissue. VICTOR C. MYERS and MORRIS S. FINE (*J. Biol. Chem.*, 1915, **21**, 583—599).—Creatine is transformed into creatinine, and vice versa, even in pure solutions, at a constant rate, which represents 0·5% per day at body temperature. In autolysing muscle, the change of creatine to creatinine is more than three times as rapid, a rate which compares with that of the formation of creatinine in the body. Since the creatinine is removed by the kidneys almost as rapidly as it is formed, the transformation in the body must proceed at maximum intensity; a high temperature during autolysis, or in the body (fever), has the same effect. Creatine added to autolysing muscle undergoes the same fate, but added creatinine inhibits the reaction or reverses it. In autolysis there is no destruction of the substance; the question of enzyme action is postponed. In autolysing blood (human), there is increase in both creatine and creatinine, and the same is true for rabbit's liver. In the bird, the metabolism is different, for there creatine, not creatinine, is excreted in the urine, and creatinine is not absent from the blood, and autolysis of muscle shows no difference from that seen in mammals. The following view is taken of the metabolic significance of the observations. Creatinine is present in muscular tissue in higher concentration than in other tissues; this suggests that muscle is the seat of creatinine formation; most of the creatine in the body is present in muscle also; this substance has a definite concentration in a given species of animal, and during an autolysis is converted into creatinine at a constant rate. If this reaction occurred *in vivo*, the well-known constancy of creatinine elimination would be explained. Since the muscle creatine and the urinary creatinine are constant, there must be a definite ratio between the two. This would be the equivalent of a daily conversion of creatine to creatinine of about 2%. When creatine is administered to men or animals, the conversion into creatinine corresponds very well with this figure, and the same rate is seen in autolysing muscle. In fevers there is a definite relationship between the rise of temperature and creatinine excretion; the same influence on the formation of creatinine is seen in autolysis when the temperature is raised. W. D. H.

Physiology of Lactation. W. L. GAINES (*Amer. J. Physiol.*, 1915, **38**, 285—312).—Transfusion of blood from a pregnant to a lactating goat temporarily inhibits the secretion of milk. Extracts of the placenta and mammary gland from a pregnant cow

have the same effect. Transfusion of blood from a heavy-milking goat into a low-milking one fails to accelerate the secretion. Pituitrin acts on the muscular tissue of the mammary gland even in an excised gland. Nursing, milking, and the insertion of a cannula into the duct excite reflexly this muscular tissue, and this does not occur during anæsthesia. The loss of volume in the udder after milking is nearly equal to that of the milk drawn. Passing milk through a filter separates it into fractions of different fat-content. Physical filtration may account in part for the rise in fat-content of the milk with progress in milking. W. D. H.

Some New Constituents of Milk. I. Phosphatides. THOMAS B. OSBORNE and ALFRED J. WAKEMAN (*J. Biol. Chem.*, 1915, **21**, 539—550).—Knowing that milk contains all the nutrients necessary for growth, and recognising that its proteins, fats, carbohydrates, and salts are not all sufficient, the knowledge of all constituents, present in however small amount, is thus a matter of special importance. Working as the authors have done with thousands of litres, the possibility of dealing with these has not been missed, and the present paper deals with the phosphatides the existence of which in milk has been denied by some workers. Brodrick-Pittard (*Biochem. Zeitsch.*, 1914, **67**, 382) affirms there are two phosphatides in it, and this is confirmed. They can be isolated from alcoholic extracts of the coagulum obtained by boiling the milk serum after the caseinogen has been precipitated by dilute hydrochloric acid. One is a monoamino-monophosphatide resembling the typical lecithin (stearyl-oleyl lecithin) of the text-books. The other is a diamino-monophosphatide resembling Dunham's carnaubon. These are possibly combined with protein, not lactalbumin, but some other protein. W. D. H.

The Catalase Reaction of Milk. H. B. TAYLOR (*J. Roy. Soc. New South Wales*, 1914, **48**, 319—332).—The accelerating action of milk on the decomposition of hydrogen peroxide is attributable to the presence of the enzyme, catalase. The catalysis of hydrogen peroxide by this means is shown to be a reaction of the first order, but the velocity constants vary very greatly with samples of milk of different ages, K having a maximum value when the milk is about twenty-two hours old. The initial increase is probably due to the production of catalase in the milk by bacteria derived from the udder or from the air, and the subsequent decrease to the inhibitive action of lactic acid. Pure catalase solution, prepared from milk by precipitating the caseinogen with acetic acid, and the enzyme by adding alcohol to the filtered solution, and subsequently treating it with water in the presence of chloroform, readily decomposed hydrogen peroxide, and the rate of decomposition was proportional to the concentration of the enzyme. The reaction was not a typical first-order reaction, as increase in the concentration of the hydrogen peroxide caused a decrease in the value of K, showing that it has an inhibiting influence on the action of the enzyme. The value of the tempera-

ture-coefficient for the range 0—15° is 1·47, a figure which agrees with that given by Senter for blood catalase (A., 1903, ii, 661). The optimum temperature is in the vicinity of 25°. Tables are given showing the effect of increase of temperature and increase in concentration of hydrogen peroxide on the rate of inactivation of the catalase calculated from Tammann's formula (A., 1896, ii, 243). The rate of inactivation is thus shown to be two and a-half times as fast at 15°, and two hundred times as fast at 50°, as it is at 0°. The effect of potassium cyanide and hydrogen cyanide on a dialysed solution of milk catalase was also observed. The behaviour of these substances was quite different from that of hydrogen peroxide, for although they decrease the activity of the enzyme (decrease in K), yet they increase its stability (decrease in K_E, the rate of inactivation), and hence more hydrogen peroxide is actually decomposed with increasing concentrations of cyanide. The effect in these directions of hydrogen cyanide was about ten times as great as that of the equivalent amount of potassium cyanide. The author draws the conclusion that the catalase of milk is analogous to that obtained from the blood. G. F. M.

A Complement-stimulating Substance in Cow's Milk. R. T. Hewlett and C. Revis (*J. Hygiene*, 1915, **15**, 1—10. Compare this vol., i, 70).—The substance which acts as complement in milk shows certain characters which lead to doubt as to its true nature; it is, however, definitely shown by the experiments recorded that the hæmolytic system (heated ox-serum, guinea-pig's corpuscles) is of a peculiarly sensitive character in regard to ox-complement in the presence of milk. W. D. H.

Physico-chemical Researches on Animal Liquids. IX. Curve of Neutralising Force of Urine. G. Quagliariello and E. d'Agostino (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 638—645). Compare A., 1912, ii, 185, 1158).—The authors have traced the curves of neutralising force of a normal urine, an artificial urine of the composition given by Meyer (Neuberg's Handbuch, "Der Harn, etc.," 1911, 4), and of a solution of 0·05 mol. of potassium dihydrogen phosphate per litre, this corresponding approximately with the mean concentration of the phosphoric acid in urine. For greater (negative) values of $\log[H^{\cdot}]$ than -6, the curves for the natural and artificial urines are almost parallel, equal additions of acid or alkali producing equal variations in the reaction. But for smaller values of $\log[H^{\cdot}]$ than -6, these two curves differ markedly, the neutralising force of the artificial urine being considerably lower than that of the physiological liquid. The curves for the artificial urine and for phosphoric acid exhibit great similarity.

The differences here observed between natural and artificial urines may depend on: (1) the presence of small proportions of organic components of which little is known, particularly as regards their physico-chemical behaviour, or (2) the fact that urine does not contain in a pre-formed condition all the constituents deter-

mined by chemical analysis. Since organic compounds of which little is known occur in urine in only minute proportions, the authors regard the second of these explanations as the more probable. T. H. P.

Creatinuria. ALONZO ENGLEBERT TAYLOR (*J. Biol. Chem.*, 1915, **21**, 663—665).—In two children, one suffering from hypopituitarism, the other from recurrent vomiting, creatine was found in the urine; this was not explicable as due to interference in the colour reaction of acetone substances, or to deficiency of carbohydrate in the diet; the figure for urinary ketones was normal in the first case and low in the second. In four normal children creatine was also found. In the child, creatine is only incompletely transformed into creatinine. W. D. H.

The Wassermann and Luetin Reactions in Leprosy. W. FLETCHER (*J. Hygiene*, 1915, **15**, 102—128).—Certain cases of leprosy give the Wassermann reaction, and this does not appear to be always due to antecedent syphilis. Leprosy does not cause the luetin reaction to become positive. W. D. H.

Sterilisation of Vaccines. F. E. TAYLOR (*J. Hygiene*, 1915, **15**, 163—168).—Sterilisation by exposure to ultra-violet rays is uncertain. Heating is recommended, and even boiling does not destroy the antigenic and immunising powers of staphylococcal vaccines; less satisfactory results were obtained by the addition of antiseptics. W. D. H.

The Action of Anæsthetics in Preventing Increase of Cell-permeability. J. F. MCCLENDON (*Amer. J. Physiol.*, 1915, **38**, 173—179).—Anæsthetics in the concentration which retards development (2—3% alcohol or 0·5% ether) tends to inhibit the permeability-increasing action of a *N*/10-solution of sodium nitrite on the eggs and embryo of the pike (*Esox*). W. D. H.

The Action of Sodium Chloride in the Prevention of Proteotoxin Shock. HANS ZINSSER, CHARLES C. LIEB, and JAMES G. DWYER (*Proc. Soc. expt. Biol. Med., New York*, 1915, **12**, 204—208).—The protective action of a hypertonic salt solution on anaphylaxis in guinea-pigs is not due to its inhibitory action on the alexin; the protective action is also seen in animals injected with proteotoxins (Friedberger's anaphylatoxins). Dale concluded that protection in anaphylaxis is due to the decreased irritability of smooth muscle. The present paper shows that the same is true in proteotoxin shock. W. D. H.

Injurious Effect, Attributable to an Acid Intoxication, of an Exclusive Oat Diet. A. MORGEN and C. BEGER (*Zeitsch. physiol. Chem.*, 1915, **94**, 324—336).—Rabbits cannot be maintained in health on an exclusive oat diet. Addition of dicalcium phosphate or of sodium chloride to the food does not remove its injurious action;

but if calcium carbonate, or, better, sodium hydrogen carbonate, is substituted for the above salts, the diet is rendered innocuous, and the rabbits increase in weight. These results are in accord with the view that the injurious effect of the oat diet is not due to a lack of calcium salts, but to an insufficiency of basic substances in the oat to neutralise the sulphuric and phosphoric acids formed in the tissues by the oxidation of proteins. H. W. B.

Distribution of Arsenic in Liver Tissue in Cases of Poisoning. Leon A. Ryan (*J. Amer. Chem. Soc.*, 1915, **37**, 1959—1960).—Experiments with dogs on the oral or subcutaneous administration of sodium arsenite show that the arsenic is evenly distributed throughout the various lobes of the liver. J. C. W.

Chemistry of Vegetable Physiology and Agriculture.

Calcium Cyanamide Hinders Denitrification. Corrado Lumia (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 659—662).—Experiments made with an artificial nutrient solution to which potassium nitrate and soil are added show that the presence in the culture liquid of 0·15% of calcium cyanamide prevents denitrification. Thus, besides furnishing assimilable nitrogen to the soil, calcium cyanamide performs the important function of retarding the serious losses of nitrates often occurring. This observation explains the "post-humous" action of calcium cyanamide noticed during field experiments by various investigators, who found that the cyanamide exerts a more lasting and uniform effect than either ammonium sulphate or sodium nitrate. In view of the great rapidity with which the biochemical decomposition of nitrates takes place under favourable conditions, it is advisable, when nitrates are applied to the soil, to mix these with an equal weight of calcium cyanamide.

T. H. P.

The Ferments of Rum. E. Kayser (*Compt. rend.*, 1915, **161**, 181—184. Compare this vol., i, 359).—An examination of the total amount of volatile acids and the relative proportions of the three volatile acids, formic, acetic, and butyric, formed by each of the three types of yeast, bottom yeasts (I), *Schizosaccharomyces* (II), and levures à voile (III), concerned in the preparation of rum. The total acidity is higher the less acid the medium is to commence with (compare Fernbach, A., 1913, i, 231). The relative amounts of fixed and volatile acids is the same for type II whether in surface or deep cultures, but this does not hold good for the other two types of yeasts. The amount of formic acid produced increases on passing from a neutral to an acid medium, yeasts of

types II and III giving the maximum amount. The amount of butyric acid formed is highest in neutral media. The relative proportions of butyric and acetic acids produced vary with different varieties of the same type of yeast and with the nature of the medium. On the addition of nitrogenous food, yeasts of types I and II give with mineral nitrogen almost entirely acetic acid, whilst with amide nitrogen there is an increase in the formic acid, and with peptone there is only a slight diminution in the butyric acid content. These two types of yeasts give proportionately more butyric acid at 25° than at 35°. W. G.

Permanence of Certain Enzymes of Yeast. ARMINIUS BAU (*Chem. Zentr.*, 1915, i, 1216—1217; from *Woch. Brauerei*, 1915, **32**, 141—143).—The permanence of certain enzymes in fresh top and bottom yeast in similar products of 1896, dried at room temperature, and in bottom yeasts of 1903 (dried at 25°, or at 25° and subsequently at 105°), has been investigated. The results are given in the form of a table, the chief points in which are the following: invertase, maltase, and melebiase are among the most permanent enzymes; trehalase and oxydase are least stable, whilst zymase, catalase, reductase, and yeast-chymosin are sensitive and readily altered. The individual enzymes were not isolated, but used in conjunction with the dry yeast cells unless special experiment showed this to be undesirable.

Fresh yeast contains considerable quantities of zymase, invertase, maltase, melebiase, carboxylase, and catalase; endotryptase, oxydase, and reductase are less plentifully present, whilst trehalase, emulsin, amygdalase, lipase, and yeast-chymosin are only present in small quantity in German yeast.

The detection of emulsin in yeast is carried out as follows. A small quantity of dry yeast is added to a 5% solution of amygdalin and a little thymol. After twenty-four hours, the solution is filtered and distilled, and hydrocyanic acid detected in the filtrate by conversion into Prussian-blue. H. W.

Certain Antiseptic Chloro-compounds Suitable for the Treatment of Wounds. HENRY D. DAKIN (*Compt. rend.*, 1915, **161**, 150—153).—A hypochlorite solution, suitable for the treatment of wounds, since it contains no free alkali or chlorine, is best prepared as follows. 200 Grams of bleaching-powder are mixed with a solution of sodium carbonate (140 grams) in 10 litres of water. The mixture is shaken, and after thirty minutes the clear liquid is siphoned off and filtered through cotton wool. The filtrate is made just neutral or very feebly acid to phenolphthalein by the addition of boric acid. Such a solution kills *Staphylococci* in two hours at a concentration of hypochlorite below 1 in 500,000. In the presence of blood serum, the concentration must be from 1 in 1000 to 1 in 2000. Wounds can be subjected to continuous irrigation with this solution for several days without marked irritation of the skin. The solution has a high antiseptic power, possesses a certain hæmostatic action, and has the property of dissolving necrosed tissues.

Certain sodium salts of sulphonylchloroamides have been prepared and examined for the same properties. The salts tried were sodiobenzenesulphonylchloroamide, $C_6H_5 \cdot SO_2 \cdot NNaCl$, and sodio-*p*-toluenesulphonylchloroamide, $C_6H_4Me \cdot SO_2 \cdot NNaCl$. Both of these substances are strong antiseptics, and have but little toxic action. Their aqueous solution can be used in the treatment of wounds at a much higher concentration than the hypochlorites. They are not capable of dissolving necrosed tissue, and since they possess marked hæmolytic properties, must not be intravenously injected.

W. G.

Action of Radium and its Emanation on the Germination of Higher Plants. HENRI AGULHON and THÉRÈSE ROBERT (*Ann. Inst. Pasteur*, 1915, **29**, 261—273).—The results of experiments with pea seedlings subjected to the action of radiations from radium bromide contained in sealed tubes showed a decided retarding effect, less, however, than that observed by Stoklasa (*Compt. rend.*, 1912, **155**, 1096). A solution of radium bromide containing 0·001 mg., which is of the same order as the amount employed by Stoklasa, was without effect.

In a third series of experiments, different plants were grown under bell jars, both without and with radium contained in a small ebonite box covered with a piece of mica, so as to allow the emanation to diffuse. It was found that, under the influence of radium, the development of the plants was considerably accelerated. As regards the forms of the plants, the diameters of the stems at different points were somewhat diminished, whilst the distances between the knots were greatly increased. The examination of sections of the stems showed that the width of cells was greatly diminished and the length greatly increased by the action of the emanation, recalling the phenomenon of etiolation. N. H. J. M.

Formation of Hydrogen Cyanide in the Germination of Seeds. IV. CIRO RAVENNA (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 302—306. Compare this vol., ii, 381).—For the estimation of ammonia in plants, Bosshard's method, in which the aqueous extract is acidified with hydrochloric acid and treated with excess of phosphotungstic acid, and the precipitate thus obtained distilled in presence of magnesium oxide, gives results in complete accord with those yielded by Longi's method (compare Sellier, A., 1903, ii, 329; 1905, ii, 60). In order to prevent the phosphotungstic acid precipitate from passing through the filter, it is advisable, except when peptone is present, to add a little powdered talc to the liquid prior to precipitation.

The proportion of hydrogen cyanide in germinating seeds of *Phaseolatus lunatus* at first increases to a maximum, and then diminishes as germination proceeds. This behaviour is similar to that observed with other cyanogenetic seeds. T. H. P.

Direct Assimilation of Free Atmospheric Nitrogen by Plants. EVA MAMELI and GINO POLLACCI (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 966—971).—The results obtained by Oes (*Zeitsch.*

Bot., 1913, **5**, 145) and by Molliard (this vol., i, 198) do not invalidate those of the authors' experiments (A., 1910, ii, 645; 1911, ii, 759). Oes states that free nitrogen is assimilated by *Azolla*, but not by *Salvinia auriculata*, *Lemna trisulca*, *Lemna gibba*, or *Lemna polyrrhiza*; this author, however, cultivated the plants in a solution containing excessive proportions of calcium chloride, which has an injurious effect on them. With *Raphanus sativus*, Molliard obtained positive results in four cases and negative in six. This irregularity is due to: (1) the use of an unsuitable nutrient medium, 50 grams of dextrose per litre causing marked plasmolysis of the cells of the root apex; (2) insufficient food supply; and (3) estimation of the nitrogen by Kjeldahl's method, which is inapplicable to certain types of nitrogenous compounds; the authors employed Jodlbauer's modification of Kjeldahl's method.

T. H. P.

Action of Stimulants on the Development of Plants. B. Schulze (*Landw. Versuchs-Stat.*, 1915, **87**, 1—24).—Pot experiments in which sugar beets were grown in a mixed soil of sand and loam with farmyard manure, ammonium nitrate and minerals, and different manganese compounds. In every case, the application of manganese resulted in increased yields and in increased production of sugar. The greatest yield was obtained with the smallest amount of manganese nitrate (Mn = 1·2 gram per 20 kilos. of soil), whilst with larger amounts of manganese nitrate the increase was less. With other manganese compounds (except the sulphate) the yield increased with the increase in the amount of manganese. When aluminium sulphate was added to manganese sulphate, the yield rose with the increased applications. The most favourable forms of manganese seem to be the phosphate and (with aluminium sulphate) the sulphate. In a mixture of hydroxide and carbonate as much as 12·2 grams per 20 kilos. of soil had no injurious effect.

The results of pot experiments in which oats, mustard, and peas were manured with "radioactin" showed that the application of this substance resulted in increased yields, fruit production being especially increased. The results seem to be due to stimulation only, without increased assimilation of nutrients.

"Radioactin" consists mainly of aluminium silicate, containing only a small amount of radium salt and relatively large amounts of thorium. The amounts employed were approximately 0·02 to 0·2 gram per kilo. of soil. With the lowest and highest amounts the yields of oat grain were increased by 7·7% and 17·8% respectively. In practice, however, the cost would be considerable.

N. H. J. M.

Presence in Plants of Hæmatoid Compounds of Iron. I. G. Gola (*Atti R. Accad. Lincei*, 1915, [v] **24**, i, 1239—1243).—By extraction with sodium carbonate solution, and subsequent precipitation by means of acetic acid, the author has obtained from sawdust, bark, the leaves of *Parietaria officinalis*, dried but non-

fermented grass, beer-yeast, *Lactarius controversus*, and *Penicillium glaucum*, a brown, amorphous substance rich in iron, which is, however, detectable only after incineration. This substance may be purified by dissolution in solutions of sodium hydrogen carbonate or borax, and precipitation by acidification. Treatment with potassium hydroxide at 200—240° in absence of air, extraction of the alkaline mass with absolute alcohol, addition of glycerol and ether to the alcoholic solution, and addition of ether and acetic acid to the glycerol solution, result in the separation of a brown, amorphous compound, almost insoluble in neutral solvents, but soluble in pyridine. This compound yields a brown, amorphous, readily soluble picrate, which melts easily and burns with a slight deflagration, giving a luminous flame. The iron may be detached from the organic part of the molecule slowly by acetic acid, and more rapidly by aqueous alkali.

Four different compounds appear to be obtainable from the materials named above, the first being soluble in alkaline alcohol, the second in glacial acetic acid, the third insoluble, and the fourth inorganic. These may correspond with four distinct compounds existing in the plant, or may be the result of an incomplete action in the fusion with potassium hydroxide.

From the results obtained, it seems likely that the condition of the metal in these compounds is analogous to that of the metal in hæmatin, and this is borne out to some extent by comparison of the spectroscopic characters of the compounds with those of the compound obtained from ox-blood by the methods described above.

T. H. P.

Permeability. I. Exosmosis of Electrolytes as a Criterion of Antagonistic Ion Action. WALTER STILES and INGVAR JØRGENSEN (*Ann. Bot.*, 1915, **29**, 349—367).—Twenty discs of potato, 1 cm. in diameter, weighing about 0·5 gram, were washed in distilled water, dried on filter paper, and placed in 100 c.c. of solution, the conductivity of which was measured from time to time. In some experiments, living bean plants were used. The substances employed as external medium included both poisons and nutritive salts, and were used in concentrations of $N/1000$. No qualitative difference was observed between the behaviour, as regards permeability to electrolytes, of potato discs and the roots of entire bean plants, which seems to indicate that the methods are suitable for general use.

It seems reasonable to assume that, within certain limits, the rate of exosmosis is a measure of toxicity. A decrease in this rate when certain ions are added to solutions containing poisonous ions might be due to the same cause that produces what is called antagonism. Attention is called to the complexity of the phenomena and to the necessity of considering each case separately. Results obtained at different temperatures should be carefully analysed before conclusions can be drawn. N. H. J. M.

The Osazone Method of Locating Sugars in Plant Tissues. SYDNEY MANGHAM (*Ann. Bot.*, 1915, **39**, 369—391).—The plant tissues

are placed in a glycerol solution of phenylhydrazine hydrochloride and sodium acetate, and heated for an hour at 98—100°. Some diffusion of cell contents may occur during the heating, but this will be less than when aqueous reagents are employed. Lævulose very readily yields an osazone, and in preparations heated for half an hour, crystals, frequently arranged in sheaves, are often formed before cooling. Dextrose may fail to give positive results if present in very small concentrations. The crystals are usually shorter, and form spherical clusters. Sucrose, when present in sufficient quantity, may be partly hydrolysed during the heating; the yield of crystals is, however, much less than with dextrose.

Maltose, when heated for an hour, forms a golden-yellow syrup, from which crystals may form. The production of such syrup inside starch-forming cells which have been treated with Senft's reagent probably indicates the presence of maltose.

N. H. J. M.

Stereochemistry and Biological Action of Ammonium Compounds. F. Plate (*Atti R. Accad. Lincei*, 1915, [v], **23**, ii, 292—296. Compare this vol., i, 487).—In concentrations of $N/50$—$N/3200$, ammonium nitrate exerts an injurious influence on *Avena sativa*, whereas ammonium chloride favours the development to some extent. This is probably due to the fact that the nitrate is less dissociated than the chloride, so that its less dilute solutions contain free hydrogen ions, which arrest root development (*loc. cit.*).

T. H. P.

The Presence of Choline in the Shoots of Aralia cordata. K. Miyake (*J. Biol. Chem.*, 1915, **21**, 661—662).—In addition to guanine and xanthine (this vol., i, 758), these shoots also contain choline.

W. D. H.

The Active Substance in Baccharis coridifolia (Mio-Mio). J. Brandl (with G. Schaertel) (*Arch. Pharm.*, 1915, **253**, 195—201).—This is a plant which grows to a large size in Argentina, and is avoided by animals except in the last extremity of hunger. The leaves and flowers are very toxic, the chief symptom being acute gastro-enteritis. It was used by the Indians, under the name Mio-mio, as a drug, and is still frequently used in blistering ointments, the action being as powerful as that of cantharides.

Arata (1877) extracted the plant with amyl alcohol in the presence of lime, and obtained a crystalline substance, which he called "baccharin," and assumed to be an alkaloid. It is now found that amyl alcohol does extract a crystalline compound, but that it is not toxic. The real active principle was found in a light petroleum extract. The concentrated solution was treated with alcohol, which precipitated a non-toxic resin and a non-toxic white *compound*, $C_{20}H_{42}O$, needles, m. p. 80°, which could not be oxidised, brominated, or acetylated, whilst the residual *baccharis oil* (10 grams from nearly 2 kilos. of the dried plant) was very

active. Sodium carbonate and dilute sulphuric acid only removed small amounts of non-poisonous substances, but the toxicity was destroyed by sodium hydroxide. J. C. W.

Constituents of Gloriosa superba. HUBERT WILLIAM BENTLEY CLEWER, STANLEY JOSEPH GREEN, and FRANK TUTIN (T., 1915, **107**, 835—846).—An examination of the extracts of the dried tubers of *Gloriosa superba*, Linn., from Ceylon, has revealed the presence of the following definite compounds, in addition to amorphous products and an enzyme, which readily hydrolyses amygdalin: (1) benzoic acid; (2) salicylic acid; (3) *2-hydroxy-6-methoxybenzoic acid*, m. p. 135°, which gives a violet coloration with ferric chloride, and on methylation yields *methyl 2 : 6-dimethoxybenzoate*, long, colourless needles, m. p. 88°; the identity of this acid was established by the preparation of the last-named ester from the crude mixture of 2 : 4- and 2 : 6-dihydroxybenzoic acids resulting from the interaction of resorcinol with water and ammonium carbonate at 120—130°, by vigorous methylation with methyl sulphate and potassium hydroxide, and subsequent heating with alkali in alcoholic solution, when the ester of 2 : 6-dimethoxybenzoic acid remained unhydrolysed; (4) choline; (5) dextrose; (6) palmitic acid and a mixture of unsaturated acids; (7) small amounts of a hydrocarbon, m. p. 63—65°, and a fatty alcohol, m. p. 77°; (8) a mixture of phytosterolins, containing stigmasterol glucoside and probably sitosterol glucoside; (9) a mixture of phytosterols, which contains stigmasterol and probably sitosterol; a mixture of alkaloids consisting chiefly of (10) colchicine, which is present in the drug to the extent of 0·3%, and has hitherto been known to occur only in *Colchicum*, together with small amounts of (11) an *alkaloid*, $C_{33}H_{38}O_9N_2$ or $C_{15}H_{17}O_4N$, pale yellow leaflets, m. p. 177—178°; and (12) an *alkaloid*, $C_{23}H_{27}O_6N$ (?), long, colourless needles, m. p. 267°.

Colchicine crystallises from ethyl acetate in small, soft, pale yellow needles, m. p. 155—157°, has $[\alpha]_D^{16\cdot5}$ −121·3° in chloroform, and forms an *aurichloride*, soft, yellow needles, m. p. 209°. The toxic properties of *Gloriosa* tubers are due, essentially, to this constituent. F. B.

The Distribution of Cyanogen in Grasses, Especially in the Genera Panicularia or Glyceria and Tridens or Sieglingia. CARL L. ALSBERG and OTIS F. BLACK (*J. Biol. Chem.*, 1915, **21**, 601—609).—Twenty-two species of American grasses were examined. Cyanogen was found in *Tridens flavus*, *Panicularia nervata*, *P. grandis*, and *P. canadensis*. Three other American species of *Panicularia* did not contain it. *Stipa Vaseyi* (sleepy grass of the south-west), generally regarded as poisonous, did not contain cyanogen. W. D. H.

The Blackening of the Leaves of the Wild Indigo (Baptisia tinctoria) and the Isolation of a New Phenol, Baptisol. ERNEST D. CLARK (*J. Biol. Chem.*, 1915, **21**, 645—660).—Substances of the

ester type and acetone are more active in producing the blackening than volatile antiseptics, such as chloroform, ethyl ether, and toluene, but any agency that disturbs the normal relationships of the cells containing enzymes and those containing the substrate has the same effect. Probably a hydrolytic enzyme decomposes a glucoside, and then an oxydase produces the pigment. A new phenol, *baptisol*, was isolated from the efflorescence on the dried leaves blackened by vapour of chloroform, etc. It has the formula $C_{15}H_{12}O_5$ and m. p. 213° (corr.). *Triacetylbaptisol*, $C_{15}H_9O_5Ac_3$, has m. p. 189° (corr.); *tribenzoylbaptisol*, $C_{15}H_9O_5Bz_3$, has m. p. 183° (corr.). This indicates three hydroxyl groups; it also contains one methoxyl group, and the formula $OMe{\cdot}C_{14}H_6O(OH)_3$ is suggested. Baptisol is not identical with either of the other two phenols (butin and naringenin) with the same formula which have been described. W. D. H.

Mulberry Leaves: Chemical Composition in the Morning and Evening. II. Luciano Pigorini (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 433—437. Compare *Atti R. Ist. Veneto*, July, 1914).—Analyses have been made of mulberry leaves gathered in the morning and evening between September 7th and 16th. The proportions of water and of protein and non-protein nitrogen found are less, and those of dry residue greater, than with spring or summer leaves. As is the case with other plants, the leaves accumulate carbohydrates, fats, proteins, and other nitrogenous compounds under the influence of sunlight, leaves gathered in the evening being, therefore, the richer in nutrient substances. T. H. P.

Secretions. C. Mace. A. Tschirch and H. Schklowsky (*Arch. Pharm.*, 1915, **253**, 102—109).—Although the essential oil of nutmeg has been fairly completely investigated (compare Power and Salway, T., 1907, **91**, 2037), little is known of the carbohydrates, dyes, and "fats" (*ibid.*, 1908, **93**, 653).

Finely powdered mace has now been exhausted by light petroleum, alcohol, chloroform, and, finally, water. The brown oil contained in the first extract gave a large deposit of crystals on cooling. These were obtained, after forty to fifty crystallisations from alcohol, in colourless leaflets, m. p. 70°. The compound was recovered unchanged after boiling with potassium hydroxide, and was proved to be neither a glyceride nor a phytosterol, but an acid. It is designated *macilenic acid*, has the formula $C_{14}H_{26}O_2$, the iodine number 111·03, forms well-defined *silver*, *barium*, and *potassium* salts, and belongs to the oleic acid series.

The remaining oil was mixed with a little potassium hydroxide and submitted to steam distillation for a week. The residual liquid consisted of two layers, the supernatant one containing a small amount of the potassium salt of (?) myristic acid. Special search was made for glycerol, but none could be found. The authors believe that mace does not contain a true fat. When distilled under reduced pressure, the oil, freed from macilenic acid, gave a fraction, b. p. 280—290°, which solidified on cooling, and

crystallised in pearly scales, m. p. 68°. This is a saturated acid of the lanopalmitic series, designated *macilolic acid*. It has the formula $C_{20}H_{40}O_3$, and forms a *silver* salt.

The alcoholic extract contained much colouring matter, waxes, and a colourless substance, m. p. 76—77°. The chloroform extract contained a phytosterol, m. p. 131°, insoluble in alcohol, and a fairly pure *dye* with deep reddish-yellow colour. The aqueous extracts were still yellow, and contained an amylodextrin of the formula $6C_6H_{10}O_5,2H_2O$. J. C. W.

Oil of the Seeds of Strychnos nux vomica. II. A. Heiduschka and R. Wallenreuter (*Arch. Pharm.*, 1915, **253**, 202—213. Compare A., 1912, ii, 1087).—The unsaponifiable portion of the oil has been examined more fully. The material was separated by the method of Matthes and Heintz (A., 1909, i, 572) into a resinous portion, a phytosterol with m. p. 158°, and a saturated *alcohol*, $C_{35}H_{57}\cdot OH$ or $C_{35}H_{59}\cdot OH$. The latter crystallises in silky tufts from *iso*butyl alcohol, m. p. 188°, α^{15} + 90°, and forms an *acetate*, m. p. 223°, α^{15} + 74·47°; a *propionate*, leaflets, m. p. 215°; a *benzoate*, stellar aggregates, m. p. 197°; and a *salicylate*, leaflets, m. p. 238°. The acetate was oxidised by chromic acid and glacial acetic acid to, apparently, oxyamyrin acetate, $C_{32}H_{50}O_3$.

Another alcohol was isolated by dissolving the original substance in acetic anhydride. The impure acetate of the above alcohol crystallised first, followed, after a day or two, by the *acetate*, colourless leaflets, m. p. 123—124°, of an unsaturated *alcohol*, $C_{32}H_{54}O,\frac{1}{2}H_2O$, m. p. 99°, which behaved like sycoceryl alcohol. J. C. W.

Biochemistry of Sea Weeds. Harald Kylin (*Zeitsch. physiol. Chem.*, 1915, **94**, 337—425. Compare A., 1913, i, 435).—The author has isolated and compared the various constituents of seaweeds belonging to the orders *Fucoideae* and *Florideae*.

Nitrogen is present as ammonia in all seaweeds, and occurs also as nitrate in some and not in others of those examined. Phosphorus is found as phosphate in the young parts of the thallus, but not in recognisable quantity in the older portions of the *Fucoideae*. Iodine, as iodide, is similarly distributed, and also occurs as free iodine or as a labile iodine compound in the *Florideae Bonnemaisonia asparagoides* and *Spermothamnion roseolum*. Calcium is a constant constituent of the cell walls of all seaweeds, and is usually combined with pectic acids. Free organic acids are not present in the cells of *Fucoideae* or of *Florideae*, but traces of oxalates are sometimes found. Several *Fucoideae* contain from 5·2 to 6·8% of mannitol.

The *Florideae* contain traces of free dextrose, whereas maltose, sucrose, and lævulose are absent. Some of them also contain considerable quantities (up to 10% of the dried material) of trehalose. In the *Fucoideae*, dextrose is found in traces, but trehalose is absent. Instead, a lævorotatory disaccharide is present, which is termed *laminariose*. It has not been isolated.

Laminarin (*loc. cit.*) is shown to consist, not of a single polysaccharide, as first described, but of a series of closely related polysaccharides with specific rotations varying from $-7°$ to $-32·5°$. With a rise in the numerical value of the specific rotation, there is a fall in the molecular weight, an increase in the solubility in water, and a decrease in the precipitability with alcohol. The lowest member of the series is laminariose, $2C_6H_{10}O_5,H_2O$.

Laminarin constitutes 35% of the dried *Laminaria digitata*. Other *Fucoideae* contain from 7 to 33·4% of laminarin. Laminarin is hydrolysed by malt diastase, yielding dextrose. It constitutes a reserve foodstuff analogous to starch, which is built up in the thallus during the summer and utilised by the seaweed for growth and reproduction during the winter, so that the young leaves in the spring are devoid of the material.

The constituents of the cell walls of the *Fucoideae* are: (1) fucoidin, $[\alpha]_D -220°$; on hydrolysis forms fucose; (2) algin, the calcium salt of *algic acid*, $[\alpha]_D -136°$; (3) fucin, the calcium salt of *fucic acid*, $[\alpha]_D -120°$, coloured blue by iodine in potassium iodide solution containing 1% of sulphuric acid; and (4) cellulose. The possible physiological functions of these various substances are discussed. H. W. B.

The Amino-acid Content of Certain Commercial Feeding Stuffs and Other Sources of Protein. E. H. NOLLAU (*J. Biol. Chem.*, 1915, **21**, 611—614).—It is probable that in the future, protein-feeding will be based on amino-acid make-up. Hence the present analyses. The results, given in a table, show many marked differences between proteins and protein-containing foods. For example, histidine is absent in distillers' dried grains and the cow-pea; non-amino-nitrogen is absent in wheat bran and maize kernel. Lysine is abundant in soja bean, distillers' dried grains, wheat bran, dried blood, maize kernel, hemp seed, and sunflower seed, and absent in rice, oats, and barley. Mono-amino-acids constitute in most cases 50% of the amino-acids present. The high ammonia content and the low lysine content of gluten are marked. Peanut, black walnut, and hickory nut are rich in arginine and poor in histidine; the reverse obtains in the pecan. W. D. H.

Organic Chemistry.

Vapour Pressures of Propane, Propylene, and *n*-Butane at Low Temperatures. G. A. Burrell and I. W. Robertson (*J. Amer. Chem. Soc.*, 1915, **37**, 2188—2193).—In an earlier paper (this vol., i, 861), the authors determined the vapour pressures of ethane and ethylene at low temperatures. The same method has now been applied to propane, propylene, and *n*-butane with the following results. For propane, the vapour pressure ranges from 760 mm. at −44·1° to 3 mm. at −124·2°; for propylene, from 760 mm. at −47·8° to 3 mm. at −127·4°; and for *n*-butane, from 760 mm. at −0·3° to 1 mm. at −99·9°. E. G.

Trimethylethylmethane [$\beta:\beta$-Dimethylbutane] from Pinacolin. N. Kishner (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1111—1112). —*Pinacolin hydrazone*, $CMe_3 \cdot CMe{:}N \cdot NH_2$, b. p. 162°/740 mm., when heated in a sealed tube at 180° with solid potassium hydroxide and platinised porous tile, yields $\beta:\beta$-dimethylbutane. T. H. P.

Catalytic Hydrogenation I. New Method of Hydrogenation of Volatile Substances and the Rate of Hydrogenation of Ethylene. J. B. Rather and E. Emmet Reid (*J. Amer. Chem. Soc.*, 1915, **37**, 2115—2118).—A method of hydrogenating volatile substances is described in which a mixture of the volatile substance and hydrogen is passed through a non-volatile inert liquid in which the catalyst is suspended. In the experiments described, the catalyst was prepared by treating infusorial earth with solution of nickel nitrate, and adding the moist mass to a strong solution of sodium carbonate in order to precipitate the nickel as carbonate. The product was washed and dried, then reduced by heating it in a current of hydrogen, and afterwards cooled in a current of carbon dioxide. On passing a mixture of ethylene and hydrogen through melted paraffin at 180° in which the catalyst was suspended, it was found that, in the case of mixtures containing 10% of ethylene, about 70% of the ethylene was reduced when the rate of flow was 10 c.c. per minute, whilst in the case of mixtures containing a higher percentage of ethylene less regular results were obtained. E. G.

Action of Florida Earth on Unsaturated Compounds. L. G. Gurvitsch (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 827—830).—When the ethereal extract of the resinous colouring matters removed from petroleum by floridin is freed from ether by distillation and the residue added to the original decolorised petroleum, the resultant product is darker than the untreated petroleum. Since floridin contains no substances extractable by organic solvents, its action on petroleum must be accompanied by chemical change of some constituent of the petroleum. That such change consists in polymerisa-

tion of unsaturated compounds is shown by the behaviour of floridin towards amylene and the terpenes.

When freshly rectified amylene, b. p. 39—40·5°, is mixed with an equal weight of dehydrated floridin, a considerable rise of temperature occurs; after two hours, about 15% and after two days, about 85% of polymerised products, b. p. above 100°, are formed, these consisting largely of the diamylene obtainable by the action of sulphuric acid on amylene.

In the case of pinene, the addition of 5% of floridin causes vigorous boiling and a larger proportion may occasion the projection of the whole of the liquid from the containing flask. After careful treatment of a specially purified sample of pinene, b. p. (98%) 154·8—157·9°, D_{18}^{18} 0·8627, $[\alpha]_D$ −39·6°, with 25% of floridin, a liquid, D_{18}^{18} 0·8928, $[\alpha]_D$ −5·0°, was obtained. Fractionation of the latter gave 6—7% of camphene, calculated on the weight of the original pinene; this yield is capable of being increased considerably. No dipentene was found, but 37% of the treated liquid, b. p. above 200°, apparently consists of sesqui- and poly-terpenes.

Polymerisation of amylene is effected also by carbon and by alumina, the development of heat in the latter case being more marked than with floridin. In the case of pinene, no other absorbent causes polymerisation and isomerisation; addition of blood charcoal or alumina is accompanied by generation of comparatively little heat, the pinene remaining unchanged. T. H. P.

Interaction of Dimercuriammonium Nitrite and the Alkyl Iodides. Prafulla Chandra Ray (T., 1915, **107**, 1251—1254).—The action of alkyl iodides on dimercuriammonium nitrite gives rise to nitrogen, mercury, mercurous iodide, and, in addition, an alkyl nitrite and a nitroparaffin in nearly equal quantities. This result is in harmony with the idea that the mercury compound should decompose initially according to the equation

$$2NHg_2NO_2 = N_2 + 2Hg + 2HgNO_2$$

(compare T., 1910, **97**, 324), the mercurous nitrite then reacting with the alkyl iodide, as the author has previously shown, with formation of a nitrite and the isomeric nitro-compound. The course of the reaction was quantitatively studied with methyl, ethyl, and *iso*propyl iodides, the nitrite was absorbed in alcohol and estimated volumetrically, and the nitro-compound was in each case identified. G. F. M.

The Conversion of Aliphatic and Aromatic Sulphonic Acids into Aldehydes and Phenols. John H. Mandel and Carl Neuberg (*Biochem. Zeitsch.*, 1915, **71**, 180—185).—By the action of hydrogen peroxide in the presence of minute amounts of a ferric salt, scission of the sulphonic acid group in the form of sulphuric acid readily takes place from these substances. Ethanesulphonic acid yields, in addition to sulphuric acid, when submitted to this treatment, acetaldehyde, whereas aminoethanesulphonic acid (taurine) yields aminoacetaldehyde, benzenesulphonic acid yields phenol, resorcinol and catechol, and toluene-ω-sulphonic acid yields benzaldehyde. The yield was not sufficiently good for the employment of this method as a general one for the preparation of aldehydes and phenols. S. B. S.

Hexyl*iso*amylcarbinol. I. VANIN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1094—1101).—It has been already shown (A., 1913, i, 1296) that nickel carbonate forms an excellent reagent for the removal of hydrogen chloride from the chlorohydrin of β-methyl-ε-propyloctan-ε-ol. It is now found that a similar means serves for the removal of hydrogen chloride from ε-chloro-β-methylundecane.

*Hexyliso**amylcarbinol** (β-methylundecan-ε-ol)*,

$$CH_3\cdot[CH_2]_5\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CHMe_2,$$

obtained, together with heptyl alcohol, by the action of magnesium *iso*amyl bromide on heptaldehyde, is a viscous liquid, solidifying in snow and salt, b. p. 130—133°/20 mm., D_0^0 0·8392, D_0^{20} 0·8255, and has the normal molecular weight in boiling benzene. With phenylcarbimide it reacts with marked heating, giving a crystalline product.

The formation of heptyl alcohol is explained on the assumption that the reaction proceeds in two different directions (R = C_6H_{13}):

(1) $R\cdot CHO + C_5H_{11}\cdot MgBr = C_5H_{11}\cdot CHR\cdot OMgBr$,

and (2) $= CHRBr\cdot O\cdot Mg\cdot C_5H_{11}$. Decomposition of the latter complex by water yields the primary heptyl alcohol,

$$CHRBr\cdot O\cdot Mg\cdot C_5H_{11} + H_2O = CH_2R\cdot OH + MgBr\cdot OH + C_5H_{10}.$$

A number of similar cases are quoted.

ε-Chloro-β-methylundecane, $C_{12}H_{25}Cl$, prepared by saturating the corresponding alcohol with dry hydrogen chloride, was not obtained in a pure state. When boiled with nickel carbonate in a reflux apparatus, it yields a *hydrocarbon*, $C_{12}H_{24}$, b. p. 204—206°/753 mm., which may be either β-methyl-Δ^{δ}-undecene, $CH_3\cdot[CH_2]_5\cdot CH{:}CH\cdot CH_2\cdot CHMe_2$, or β-methyl-$\Delta^{\epsilon}$-undecene, $CH_3\cdot[CH_2]_4\cdot CH{:}CH\cdot CH_2\cdot CH_2\cdot CHMe_2$.

T. H. P.

Simple Isomeric Changes of the Glycols and their Nitrogenous Derivatives. II. Formation of Propaldehyde and Acetone from Propylene Glycol, Propylenediamine, Trimethylene Glycol, and Trimethylenediamine. CARL NEUBERG and BRUNO REWALD (*Biochem. Zeitsch.*, 1915, **71**, 158—166; compare this vol., i, 214).—Propylene glycol on distillation with hydrogen peroxide in the presence of small quantities of an iron salt yields acetone and propaldehyde. Propylenediamine yields the same products on treatment with nitrous acid; they can also be obtained from trimethylene glycol by the action of hydrogen peroxide and from trimethylenediamine by treatment with nitrous acid; in the last-named reaction some allyl alcohol was also obtained. The acetone was isolated in the form of its *p*-nitrophenylhydrazone and the aldehyde was oxidised by silver hydroxide to propionic acid.

S. B. S.

Synthetic Open-Chain Terpene Glycol. VIT. LONGINOV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1132—1144).—By the method of reduction of esters of tribasic acids previously described (this vol., i, 366), glycols of the form, $OH\cdot CH_2\cdot CHR\cdot CH_2\cdot CH_2\cdot OH$, are obtained, and if the radicle of *iso*hexyl alcohol (δ-methylpentanol) is employed, the new glycol will represent a member of the βζ-dimethyloctane series.

δ-Methylpentanol, $CHMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$ (compare Rossi,

Annalen, 1865, **133**, 180; Bouveault and Blanc, A., 1905, i, 13), prepared by converting *iso*amyl alcohol, through the corresponding bromide and nitrite, into β-methylvaleric acid and reducing the ethyl ester of the latter in alcoholic solution by means of sodium, has b. p. 151—152°/747 mm., D_4^{20} 0·8156, n_D^{20} 1·4142. *iso*-Hexyl iodide (α-iodo-δ-methylpentane) is a colourless, mobile liquid, b. p. 172—174°/769 mm., 69·5—70°/23 mm., D_4^{20} 1·4283, n_D^{20} 1·4892, with a characteristic, pleasant odour.

Ethyl ζ-methylheptane-αγγ-tricarboxylate,

$$CO_2Et\cdot CH_2\cdot C(CO_2Et)_2\cdot[CH_2]_3\cdot CHMe_2,$$

prepared from *iso*hexyl iodide and ethyl β-sodioethane-αββ-tricarboxylate, forms a viscous, colourless, odourless liquid, b. p. 172°/9 mm., D_4^{20} 1·0127, n_D^{20} 1·4370. The free *acid*, $C_{11}H_{18}O_6$, forms unstable crystals, m. p. 141°, and readily loses carbon dioxide, giving *ζ-methylheptane-αβ-dicarboxylic acid* (*isohexylsuccinic acid*),

$$CHMe_2\cdot[CH_2]_3\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H,$$

which forms masses of slender, acicular crystals, m. p. 73—74°.

η-Methyl-γ-hydroxymethyloctane-α-ol (*β-isohexyltetramethylene glycol*, *bupleurol glycol*), $CHMe_2\cdot[CH_2]_3\cdot CH(CH_2\cdot OH)\cdot CH_2\cdot CH_2\cdot OH$, prepared by reducing ethyl ζ-methylheptane-αγγ-tricarboxylate by means of sodium and absolute alcohol, is an odourless liquid, b. p. 160°/9 mm., D_4^{20} 0·9277, n_D^{20} 1·4555, and is accompanied by a small proportion of a compound apparently identical with the corresponding oxide (*vide infra*). Its *diacetyl* derivative, $C_{14}H_{26}O_4$, is a viscous, colourless, odourless liquid, b. p. 151—152°/9 mm., D_4^{20} 0·9660, n_D^{20} 1·4369. When heated with an excess of 60% sulphuric acid in a reflux apparatus, the glycol is converted into the corresponding *oxide*,

$$CHMe_2\cdot[CH_2]_3\cdot CH\begin{<}CH_2\cdot CH_2\\ CH_2\cdot O\end{>},$$

which is a colourless, mobile liquid, b. p. 204°/748 mm., D_4^{20} 0·8562, n_D^{20} 1·4360, with an odour resembling that of essence of lemon.

In consequence of the analogy in structure of the above glycol with the terpenic alcohol of the aliphatic series obtained by Francesconi and Sernagiotto (A., 1913, i, 283, 495) and termed bupleurol, the author suggests for it the name bupleurol glycol, which is in accord with Wallach's nomenclature for citronellol glycol.

T. H. P.

The Composition of "Lecithin." Distribution of Phosphatides in the Tissues, and Methods for their Extraction and Purification. Hugh Maclean (*Biochem. J.*, 1915, **9**, 351—377).—When phosphatides are extracted from tissues by alcohol, they always contain a nitrogenous impurity which is very difficult to remove. Many substances described as new are merely mixtures of lecithin and this substance. The latter is chemically complex and contains purine substances. The whole of the "lecithin" nitrogen is accounted for by the choline and amino-nitrogen present. "Lecithin" is a mixture in varying proportions of two somewhat similar substances, one with all its nitrogen in the form of choline (true lecithin), while the other (kephalin) has no choline but amino-ethyl alcohol instead. They may

be separated by fractionation of the cadmium chloride salt with ether. W. D. H.

Basic Copper Formates. GEORGE FOWLES (T., 1915, **107**, 1281).—When solutions of normal copper formate are boiled an emerald green, crystalline basic formate, $Cu(HCO_2)_2,2Cu(OH)_2$, is precipitated. This compound is stable in the presence of cold water but blackens when boiled with water. If dilute solutions of copper formate are heated to just below the boiling point a pale green basic salt, $Cu(HCO_2)_2,3Cu(OH)_2$, is precipitated; a compound of the same formula is also formed by bringing a solution of copper formate into contact with copper hydroxide. The compound formed in this way is pale blue in colour and tends to become gelatinous on washing. This compound is unstable in contact with solutions of normal copper formate, being converted into the green compound, $Cu(HCO_2)_2,2Cu(OH)_2$. This change is slow if cold solutions are used, but occurs rapidly on boiling. J. F. S.

Electrolytic Hydrogenation of Unsaturated Aliphatic Acids. UMBERTO POMILIO. (*Zeitsch. Elektrochem.*, 1915, **21**, 444—448).—The author has studied the cathodic reduction of unsaturated aliphatic acids. The experiments were carried out in 96% alcoholic solution containing sufficient sulphuric acid to make it 0·55N and quantities of the unsaturated acids which were equivalent with respect to their double linkings. The cathode was a nickel gauze cylinder coated with spongy nickel and the anode a platinum wire. A voltage of 10—20 volts and a current of 0·5 ampere were employed. The rate of reduction was deduced from the rate of depolarisation of the cathode by the acid, and this was deduced by comparing the volumes of hydrogen liberated at the cathode with the volume of hydrogen liberated in the same time in an acid voltameter. It is shown that crotonic, Δ^{γ}-pentenoic, fumaric, maleic, mesaconic, citraconic, itaconic, allylmalonic, and aconitic acids are speedily reduced to saturated acids; but that the acids, oleic, erucic, ricinoleic, linoleic, and undecenoic are reduced only to a slight extent or in some cases not at all. The configuration of the acids in relation to the ease with which they are reduced is discussed. J. F. S.

Isomerism of Erucic, Brassidic, and *iso*Erucic Acids. III. Their Reciprocal Cryoscopic Behaviour. IV. Saturation Curves of the Binary Systems. L. MASCARELLI and G. SANNA (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 30—37, 91—97. Compare this vol., i, 863).—The cryoscopic constant of erucic acid is found to have values lying between 50·5 and 53·6, the mean being 52·3, whereas Raoult's empirical law gives 209·5; van't Hoff's formula gives 12·13 cal. for the latent heat of fusion per gram-mol. The constant for brassidic acid is found to be 38·6—44·2, the mean being 41·6, the corresponding latent heat of fusion being 17·83 cal. per gram-mol. For *iso*erucic acid, the mean cryoscopic constant is 52·54, and the calculated latent heat of fusion 13·52 cal. per gram-mol. In erucic acid, brassidic, *iso*erucic, and behenic acids are cryoscopically normal; in brassidic acid, erucic acid is normal, and *iso*erucic and behenic acids abnormal,

the latter slightly so; in *iso*erucic acid, erucic acid is normal, and brassidic and behenic acids abnormal, the former markedly so; in behenic acid, erucic acid behaves normally and brassidic and *iso*erucic acid abnormally. The fact that behenic acid does not dissolve in the solid state in erucic acid and that it does so dissolve in brassidic and *iso*erucic acids is in agreement with the observation that saturated open-chain compounds form mixed crystals with the more stable *trans*-modification of the corresponding ethylenic compound but not with the less stable *cis*-form.

The saturation curves show that: (1) Erucic and brassidic acids, erucic and *iso*erucic acids, and erucic and behenic acids do not form mixed crystals; their curves are composed of two branches, along which the pure solvent separates, and which meet in an eutectic point. (2) Brassidic and *iso*erucic acids, and brassidic and behenic acids form mixed crystals to a limited extent; the curves consist of two branches, along which mixed crystals separate. (3) *iso*Erucic and behenic acids form mixed crystals in all proportions; the curve is continuous and lies wholly between the melting points of the components. It seems probable that brassidic, *iso*erucic, and behenic acids, although they are not all isomorphs, give mixed crystals owing to phenomena of isopolymorphism. If, as with most organic compounds previously studied, the solubility in the solid state is, in this case, an index of similarity in constitution, and, with the ethylenic derivatives, in configuration, the conclusion must be drawn that erucic acid has a configuration different from those of the other acids here considered, since it is cryoscopically normal in all instances. Brassidic and *iso*erucic acids, which are soluble in the solid state in behenic acid, are similar in configuration to the latter.

These results confirm those previously obtained, but leave unexplained the existence of two *trans*-acids with ethylenic linkings. T. H. P.

Synthesis of α-Tetronic Acid. Leonore Kletz and Arthur Lapworth (T., 1915, **107**, 1254—1265).—The synthesis of α-tetronic acid (α-ketobutyrolactone) was attempted by the elimination of the oximino-group from α-oximinobutyrolactone. This substance was obtained in two forms, which are regarded as *syn*- and *anti*-isomerides, according to the source from which it was prepared, but from the *anti*-oxime only could any appreciable quantity of the free lactone be isolated. syn-α-*Oximinobutyrolactone*, $O<\begin{matrix}CO\text{—}C{:}NOH\\ CH_2\cdot CH_2\end{matrix}$, was obtained as flat prisms, m. p. 109° (decomp.), by the careful hydrolysis of *ethyl* syn-*oximino-γ-bromobutyrate* with aqueous potassium hydroxide, the latter substance being produced by the action of nitrosylsulphuric acid on ethyl ω-bromoethylacetoacetate, and forming colourless needles, m. p. 49—50°. *anti-α-Oximinobutyrolactone* was produced in 80% yield by the action of nitrous acid on ω-bromoethylmalonic acid. It is a white, crystalline substance, m. p. 192° (decomp.). With bromine it gave a brilliant blue *bromonitroso*-compound, and when reduced with tin and hydrochloric acid it was converted into α-aminobutyrolactone. When boiled with aqueous hydrochloric acid for a few minutes, it undergoes partial hydrolysis into hydroxylamine and

α-tetronic acid, since on addition of phenylhydrazine a yellow, crystalline *phenylhydrazone* of α-tetronic acid was formed, m. p. 223—224°, identical with that obtained by the action of benzenediazonium chloride on sodium ω-bromoethylmalonate. For the isolation of free α-tetronic acid, elimination of the oximino-group by treating the *anti*-oxime with sodium sulphite gave the best results. As only a small quantity of the substance could be obtained, its complete characterisation was not attempted. It formed needles or prisms, m. p. 111° (slow decomp.); with hydroxylamine the *anti*-oxime was regenerated from which it was obtained. The aqueous solution was acid to litmus, and ferric chloride gave a deep red colour.

Action of Nitrous Acid on Monoalkylmalonic Acids. [With WALTER SHARRATT.]—The action of nitrous acid on alkylmalonic acids is not generally applicable to the preparation of α-oximino-acids, but in certain isolated cases, particularly with ω-substituted alkylmalonic acids, good results can be obtained. Thus benzylmalonic acid gave a 62% yield of α-oximinophenylpropionic acid. G. F. M.

Condensation of Chloromethyl Ether with α-Alkylacetoacetic Esters. ARTHUR LAPWORTH and BENJAMIN STANLEY MELLOR (T., 1915, **107**, 1273—1280).—Condensation of chloromethyl ether with methyl sodio-α-methylacetoacetate in ethereal solution led to the formation of an *O*-substitution product of the ester *methyl methoxy-β-methoxy-α-methylcrotonate*, $OMe\cdot CH_2\cdot O\cdot CMe{:}CMe\cdot CO_2Me$, a colourless oil, b. p. 113°/18 mm., which was stable to 50% potassium hydroxide, and rapidly discharged the colour of bromine and of permanganate. With cold alcoholic potassium hydroxide, it was slowly hydrolysed to *methoxy-β-methoxy-α-methylcrotonic acid*, flat needles, m. p. 72°, which decomposed on heating with evolution of carbon dioxide, and formation of an unsaturated neutral viscid oil, b. p. 183—185°. Since this oil on heating with mineral acids decomposed into formaldehyde and methyl ethyl ketone, it is regarded as *γ-methoxymethoxy-Δ$^{\beta}$-butylene*, $OMe\cdot CH_2\cdot O\cdot CMe{:}CH\cdot CH_3$. The same decomposition products were obtained on heating the acid itself with water. A similar series of products was obtained when chloromethyl ether and ethyl sodiobenzylacetoacetate were used as starting materials. *Ethyl methoxy-β-methoxy-α-benzylcrotonate*, $OMe\cdot CH_2\cdot O\cdot CMe{:}C(CH_2Ph)\cdot CO_2Et$, was a viscid oil, b. p. 174—175°, and gave the corresponding *methoxy-β-methoxy-α-benzylcrotonic acid*, m. p. 108°, on hydrolysis. On heating the acid under atmospheric pressure, *γ-methoxymethoxy-δ-phenyl-Δ$^{\beta}$-butylene*, $OMe\cdot CH_2\cdot O\cdot C(CH_2Ph){:}CHMe$, was formed as a heavy, colourless oil, b. p. 238—240°, whilst when heated with water benzylacetone and formaldehyde were obtained.

By the condensation of methyl methoxy-β-methoxy-α-methylcrotonate with methyl acetoacetate, a crystalline *compound*, $C_{11}H_{14}O_5$, was obtained of m. p. 88—88·5°.

Ethyl acetoacetate similarly gave a *compound*, $C_{12}H_{16}O_5$, m. p. 47° The exact nature of these condensation products is still in doubt.

G. F. M.

Formation of Methylglyoxal. II. CARL NEUBERG and BRUNO REWALD (*Biochem. Zeitsch.*, 1915, **71**, 144—149).—On treatment of

various sugars with weak alkalis, methylglyoxal is formed. The reaction is carried out with 10% ammonia in closed vessels at 100° in the presence of phenylhydrazine, and methylglyoxal then separates in the form of its osazone (m. p. 147°). This substance has been prepared in this manner from the following sugars: *l*-arabinose, *l*-xylose, rhamnose, *d*-dextrose, *d*-lævulose, *d*-galactose, *d*-glucosamine, maltose, lactose, and dihydroxyacetone. The reaction can also be brought about by the use of weak alkalis other than ammonia. S. B. S.

The Behaviour of Organic Substances Containing Carbon, Hydrogen, and Oxygen towards Fehling's Solution. B. M. Margosches (*Biochem. Zeitsch.*, 1915, **70**, 252—261).—A short *résumé* of the literature on the subject. S. B. S.

Action of Alkalis on Dextrose and Lævulose. Charles Wilfrid Roberts Powell (T., 1915, **107**, 1335—1346).—Experiments depending on the measurement of the velocity of hydrolysis of ethyl acetate by sodium hydroxide in presence of varying quantities of dextrose or lævulose, and also conductivity determinations of solutions of the hydroxide in similar circumstances, indicated that these sugars unite with alkalis in equimolecular proportions to form compounds which, however, are largely dissociated into their components again by water. The degree of hydrolysis of these compounds is of the same order of magnitude. By the use of a dilatometer the velocity of the reaction between dextrose and lævulose and various alkalis was studied. The rates of decomposition of the two sugars by sodium hydroxide are equal, and it is inferred that they are each converted first into a common form, which is then decomposed at a slower rate by the alkali to form salts of various acids. The velocity coefficient for the decomposition depends essentially on the concentration of the free hydroxyl ions, although it is not exactly proportional to this. Using an excess of alkali, about 90% of the sugar disappeared after twenty-four hours' heating at 50°. G. F. M.

Biochemical Synthesis. by Means of α-Glucosidase, of the α-Monoglucoside of Ordinary Propylene Glycol. Em. Bourquelot and A. Aubry (*Compt. rend.*, 1915, **161**, 364—367*; compare this vol., i, 76).—By means of the action of α-glucosidase on an aqueous mixture of dextrose and *iso*propylene glycol, the authors have obtained a product consisting of two monoglucosides, one of which had $[\alpha]_D$ greater than +139·7° and the other $[\alpha]_D$ less than 134·7°. This mixture was readily hydrolysed by dilute sulphuric acid or by α-glucosidase, the resulting glycol being always optically inactive. The best concentration of glycol to use for the synthesis is 40 grams in 100 c.c., the enzyme being destroyed at greater concentrations. W. G.

Crystallised Starch. M. W. Beyerinck (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 305—309).—The structural characteristics of the deposits, which are obtained when starch solutions are heated for some time at about 150° and then allowed to

* and *J. Pharm. Chim.*, 1915, [vii], **12**, 283—289.

cool, suggest that the deposit is crystalline. The similarity in the optical properties of the natural starch grains and of the spherocrystals which are deposited from solution indicates that the former are built up from needle-like crystals which radiate from the dot or hilum.

Although most kinds of starch granules give rise to crystalline deposits when treated in the above manner, some behave differently. The deposits given by arrowroot afford no evidence of crystalline structure. H. M. D.

Plant Colloids. V. Soluble Starch. M. Samec and S. Jencic (*Koll. Chem. Beihefte*, 1915, **7**, 137—171; compare A., 1914, i, 930).—An account is given of the methods which have been used in the differentiation and characterisation of the various forms of soluble starch. New experiments have been made in which these physicochemical methods were applied to the examination of the soluble starches which have been prepared in different ways. In general, the formation of soluble starch is accompanied by a reduction in the size of the molecules, but this is not always the case. The varieties obtained by the method given by Malfitano and Moschkoff (A., 1910, i, 301, 817), and by heating with glycerol contain no phosphorus, but this element is present in the other forms examined.

According to Fouard, the coagulation of starch which has been "purified" by treatment with hydrochloric acid represents the reversal of the process by which soluble starch has been formed, but the authors' observations are quite inconsistent with this view. H. M. D.

Hydrocellulose. O. Hauser and H. Herzfeld (*Chem. Zeit.*, 1915, **39**, 689—670).—When hydrocellulose was extracted with boiling water, it yielded a considerable quantity of soluble copper-reducing substances; the hydrocellulose had a reducing number of 5·4 (compare A., 1907, i, 390) and this number decreased gradually until, after some seventy hours' extraction, it had fallen to 0·8. On treating the residual cellulose with 3% sulphuric acid as described by Girard, a hydrocellulose was again formed which had a reducing number of 3·9, and yielded further quantities of reducing substances. The latter appeared to consist of dextrose and dextrins (dextrose was identified by its osazone, m. p. 167°); these substances are, apparently, adsorbed in the unaltered cellulose. W. P. S.

The Oxidation of Amines. K. Suto (*Biochem. Zeitsch.*, 1915, **71**, 169—173).—Amines can be oxidised by hydrogen peroxide with the use of an iron salt as a catalyst. The experiments were carried out with the following amines: Ethylamine, *iso*amylamine, benzylamine, and aminoethyl alcohol. The following oxidation products were obtained: acetaldehyde, *iso*valeraldehyde, benzaldehyde, and glycollaldehyde and glyoxal. The aminoethyl alcohol was oxidised at the temperature of 30—50°. Higher temperatures were necessary, however, to oxidise the other amines. The products were isolated in the form of the phenylosazones or substituted phenylosazones.

Attention is called to the biological significance of these oxidation processes. S. B. S.

Influence of Double Linkings on Co-ordination Number. II. A. Pieroni and A. Pinotti (*Gazzetta*, 1915, **45**, ii, 100—106. Compare A., 1914, i, 1200).—The authors have prepared the two compounds, $CoCl_2,3C_3H_5\cdot NH_2$, and $CoCl_3,8C_3H_5\cdot NH_2$. The former behaves like an additive compound; it loses the 3 mols. of allylamine at about 60°, and dissolves in water with formation of cobalt hydroxide, the liquid assuming a marked alkaline reaction owing to hydration and subsequent ionisation of the allylamine. The second compound dissolves in cold water, giving a perfectly clear, bright red solution neutral to litmus; when this solution is heated, it loses its red colour and becomes strongly alkaline, a brown precipitate being formed. Cryoscopically, it behaves as though composed of four ions, and as both the cobalt and the allylamine are partly masked in the complex its formula should be: $[(C_3H_5\cdot NH_2)_4Co(C_3H_5\cdot NH_2)_4]Cl_3$. It would therefore appear erroneous to fix the maximum co-ordination number of cobalt as six.

The *compound*, $CoCl_2,3C_3H_5\cdot NH_2$, obtained by mixing dry allylamine with a saturated solution of cobalt chloride, previously dried at 140°, in absolute alcohol, forms red needles, and readily oxidises even in a desiccator.

The *compound*, $CoCl_3,8C_3H_5\cdot NH_2$, is prepared by the action of a current of dry air or oxygen on the previous compound either in suspension in its mother liquor or in solution in absolute alcohol. It forms minute, violet-red, acicular crystals, and decomposes without melting at 120—140°.

Two other compounds which have been obtained remain to be investigated: (1) addition of nitric acid to an aqueous solution of $CoCl_3,8C_3H_5\cdot NH_2$ yields red, acicular crystals, and (2) when these are boiled with water acidified with nitric acid they yield a heavy, red compound of siliceous appearance mixed with a yellowish substance.

In view of the high price of allylamine, the authors recommend for its preparation the following method, which gives a pure product in almost theoretical yield. One thousand c.c. of 25% hydrochloric acid and 250 grams of allylthiocarbimide are boiled in a two-litre flask fitted with a reflux apparatus until the upper layer of thiocarbimide has disappeared, and a homogeneous solution of allylamine hydrochloride is formed: $C_3H_5\cdot NCS + H_2O = C_3H_5\cdot NH_2 + COS$. The liquid is then concentrated to about one-third its volume on the water-bath, the allylamine being liberated by addition of lump potassium hydroxide, the solution being kept well cooled and mixed meanwhile. About four-fifths of the liquid is distilled, and the distillate saturated with lump potassium hydroxide in a separating funnel. The upper layer of allylamine is subjected to repeated fractional distillation over sodium until it boils completely at about 54—56°. T. H. P.

Complex Metallic Ammines. I. *cis*-Sulphonyldiacetatodiethylenediaminecobaltic Salts. Thomas Slater Price and Sidney Albert Brazier (T., 1915, **107**, 1367—1376).—Hitherto it has only

been possible to obtain complex cobalt ammines of the type $[A{:}Co\ en_2]X$, where A is the sulphito-, carbonato-, oxalato-, or malonato-radicle, that is, complexes in which either a five- or six-ring is formed by combination with the cobalt atom. Using sulphonyldiacetic acid as the dibasic acid, the authors have succeeded in obtaining a series of salts containing an eight-membered ring, these salts being of the type

$$\left[O_2S\begin{<}CH_2\cdot CO\cdot O\\CH_2\cdot CO\cdot O\end{>}Co\ en_2\right]X.$$

cis-*Sulphonyldiacetatodiethylenediaminecobaltic hydrogen sulphonyldiacetate*, $SO_2(CH_2\cdot CO_2)HY$, where $Y=\left[SO_2\begin{<}CH_2\cdot CO\cdot O\\CH_2\cdot CO\cdot O\end{>}Co\ en_2\right]$, was prepared from carbonatodiethylenediaminecobaltic bromide and sulphonyldiacetic acid by a method exactly similar to that used by Werner in the preparation of the corresponding malonato-compound (A., 1912, i, 74). It forms pink, microscopic crystals, sparingly soluble in cold water. It was found impossible to prepare other salts from this compound, owing to its sparing solubility. The *bromide*, $YBr,2H_2O$, was, however, successfully prepared by heating carbonatodiethylenediaminecobaltic bromide with one molecular equivalent of sulphonyldiacetic acid in aqueous solution, keeping the solution over night in a vacuum desiccator, and then evaporating to a low bulk on the water-bath. On cooling, the required bromide slowly separated as dull, rose-red, microscopic plates. From the bromide the following salts were obtained by the ordinary methods of double decomposition: *iodide*, YI, rose-red, microscopic crystals; *chloride*, YCl,H_2O, microscopic, rose-red plates; *nitrate*, $YNO_3,2H_2O$, pale red, microscopic prisms; *thiocyanate*, YSCN, pale brick-red, microscopic crystals; *dithionate*, $Y_2S_2O_6$, microscopic, rose-red leaflets; *platinichloride*, Y_2PtCl_6, pale brown crystals; *aurichloride*, $YAuCl_4,H_2O$, nodular masses of microscopic crystals of a burnt sienna colour.

When thiodiacetic acid was used instead of sulphonyldiacetic acid, and the attempt made to prepare thiodiacetatodiethylenediaminecobaltic hydrogen thiodiacetate, reduction of the cobalt complex took place, and a *double salt* of *cobalt thiodiacetate* and *ethylenediamine thiodiacetate*, namely $S(CH_2\cdot CO_2)_2Co,S(CH_2\cdot CO_2H)_2,C_2H_4(NH_2)_2,2H_2O$, was obtained in the form of well-developed, brownish-red, square, tabular crystals.

Oxalatodiethylenediaminecobaltic bromide was found to contain one molecule of water of crystallisation, $[C_2O_4Co\ en_2]Br,H_2O$; whereas Werner and Vilmos (A., 1899, ii, 660) describe it as anhydrous.

T. S. P.

A New Copper Compound of Glycine. J. Ville (*Bull. Soc. Chim.*, 1915, [iv], **17**, 315—318).—The products of the action of copper sulphate on glycine in the absence of potassium hydroxide vary with the molecular proportions of the two substances used. Using an excess of glycine, on the addition of alcohol, slender, blue needles of copper glycinate are obtained. Using 2 mols. of glycine to 1 mol. of copper sulphate, the addition of alcohol causes the separation of drops of a heavy, deep blue liquid, which collects at the bottom of the vessel, and is shown to be *copper glycine sulphate*, $(NH_2\cdot CH_2\cdot CO_2)Cu,H_2SO_4$. It is very soluble in water, but insoluble in alcohol, ether, benzene, and

chloroform. Allowed to remain in a vacuum desiccator, it is obtained as a transparent, hygroscopic, resinous substance. It can also be obtained by the addition of the calculated quantity of dilute sulphuric acid to an aqueous solution of copper glycinate or by the gradual addition of copper hydroxide (1 mol.) to an aqueous solution of glycine sulphate (1 mol.), followed in each case by the addition of alcohol.

W. G.

d-Lyxohexosamic Acid and $\alpha\alpha'$-Anhydromucic Acid. P. A. LEVENE and F. B. LA FORGE (*J. Biol. Chem.*, 1915, **22**, 331—335).—Of the eight possible α-aminohexoses, only glucosamine and chondrosamine are known, but of the eight amic acids, glucosamic, chondrosamic, xylohexosamic, and ribohexosamic acids have been isolated, and five of the six corresponding $\alpha\alpha'$-anhydrotetrahydroxyadipic acids have been described (compare this vol., i, 601, 782, etc.). A fifth hexosamic acid and the remaining $\alpha\alpha'$-anhydromucic acid have now been prepared.

A large quantity of *d*-galactose was prepared from lactose, converted into calcium *d*-galactonate and this into *d*-lyxose, by Ruff and Ollendorff's method (A., 1900, i, 476). The latter was left with methyl-alcoholic ammonia, and the d-*lyxosimine*, $C_5H_{11}O_4N$, m. p. 142—143°, which separated was left with aqueous hydrocyanic acid, and finally the product was hydrolysed by hydrochloric acid saturated at 0°. d-*Lyxohexosamic acid*, $C_6H_{13}O_6N$, was obtained in crystals, decomp. at about 215°, $[\alpha]_D^{25}$ – 3·58° after fifteen minutes, – 20·72° after forty-four hours. The pure acid was treated with silver nitrite and hydrochloric acid and then oxidised with nitric acid, and thus converted into inactive *$\alpha\alpha'$-anhydromucic acid*, $C_6H_8O_7$, which crystallises in long prisms from acetone, m. p. 203—204° (corr.). J. C. W.

The Decomposition of Potassium Cyanate by Heat. A. PORTEVIN (*Compt. rend.*, 1915, **161**, 308—310).—Potassium cyanate is decomposed on heating at 700—900°, yielding potassium cyanide, the decomposition increasing with rise in temperature. If potassium cyanide is added to the cyanate prior to heating, the amount of decomposition decreases as the amount of cyanide added increases.

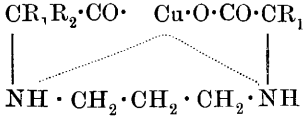
W. G.

Comparative Behaviour of Thiocarbamide and Carbamide towards Acetic Anhydride. EDWARD F. KOHMANN (*J. Amer. Chem. Soc.*, 1915, **37**, 2130—2133).—An experiment was made to ascertain whether any hydantoin would be formed if thiocarbamide was used instead of ammonium thiocyanate in the reaction described by Johnson and Nicolet (A., 1912, i, 53; 1913, i, 399) for the preparation of 2-thio-3-benzoylhydantoin. A thiohydantoin could not be detected in the product of the reaction, but a compound, m. p. 165°, was obtained which was considered to be probably acetylthiocarbamide, and it was therefore decided to prepare acetylthiocarbamide for comparison.

On heating thiocarbamide with acetic anhydride according to Nencki's method (this Journal, 1873, 1130) a mixture was obtained of acetylthiocarbamide, m. p. 165°, and *diacetylthiocarbamide*, m. p. 151—152°, which crystallises in pale yellow prisms, and probably has the structure NHAc·CS·NHAc.

When carbamide is heated with acetic anhydride, only the mono-acetyl derivative, m. p. 212°, is produced. E. G.

Tri- and Penta-methylenebis-α-imino-acids. N. A. SCHLEZINGER (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1160—1183).—The copper salts of αα′-trimethylenebisimino-acids (annexed formula), are blue, and in general resemble the copper salts of αα′-ethylenebisimino-acids (this vol., i., 506); in aqueous solution they exhibit normal molecular weights, and they are non-electrolytes. Those of αα′-pentamethylenebisimino-acids are also very stable, but they are almost, if not entirely, insoluble in water, and are violet or even reddish. According to the principle of Werner (*Neuere Anschauungen auf dem Gebiete der anorg. Chemie*, 1913, III, 246, 345, 346), and Tschugaev and Kobljanski (A., 1913, i, 1148), these salts should have the doubled molecular weight, but cryoscopic investigation of their solutions in phenol shows that the molecules are simple. These salts then form an exception to Werner and Tschugaev's principle. Although they contain in their molecule a 14-membered ring, their stability is in no way diminished.



αα′-Trimethylenedi-iminodiisobutyronitrile, $C_3H_6(NH\cdot CMe_2\cdot CN)_2$, prepared from trimethylenediamine, potassium cyanide, and acetone, forms transparent, red plates, m. p. 91—92°; its *hydrochloride*, $+2HCl$, was prepared. The corresponding *acid*, $C_3H_6(NH\cdot CMe_2\cdot CO_2H)_2$, remains unchanged in the anhydrous condition even at above 360°, and forms (1) the monohydrate, which separates in definite crystals, and (2) the dihydrate, which is obtained in flexible threads, joined at the ends to form spherical masses. The *copper* salt ($+3H_2O$) forms dark blue or, when dry, violet rhombic crystals, and has the normal molecular weight in freezing water.

αα′-Trimethylenedi-iminodiphenyldiacetonitrile, $C_3H_6(NH\cdot CHPh\cdot CN)_2$, forms rhombic plates, m. p. 97—98°. The corresponding *acid* is completely insoluble even in boiling water, and does not melt at 300°; its *copper* salt and *hydrochloride* were prepared. The *methyl* ester, m. p. 66·5—68·5°, and its *hydrochloride*, and the *ethyl* ester, m. p. 42·8—43·8°, and its *hydrochloride*, which does not melt at 230°, were prepared.

αα′-Trimethylenedi-iminodioctonitrile hydrochloride,

$$C_3H_6\{NH\cdot CH(CN)\cdot[CH_2]_5\cdot CH_3\}_2,2HCl,$$

m. p. 215—230°, begins to decompose at about 185°. The *acid*, $C_{19}H_{38}O_4N_2$, and its *hydrochloride*, *copper* salt, and *methyl* ester were prepared.

αα′-Pentamethylenedi-iminodiphenyldiacetonitrile hydrochloride,

$$C_5H_{10}(NH\cdot CHPh\cdot CN)_2,2HCl,$$

decomposes at about 141° in a sealed capillary. The acid, $C_{21}H_{26}O_4N_2$, which does not melt at 300°; its *sulphate*; *hydrochloride*; *copper* salt; *nickel* salt; *ethyl* ester, $C_{25}H_{34}O_4N_2$, obtained as a pale yellow oil; D_4^{20} 1·0775, n_D^{20} 1·5247, and its *hydrochloride* ($+2HCl$), m. p. 232° (decomp.); and *methyl* ester, which forms a viscous, pale yellow oil, D_4^{20} 1·1087, n_D^{20} 1·5353, were prepared.

aa'-Pentamethylenedi-iminodipropionitrile, $C_5H_{10}(NH\cdot CHMe\cdot CN)_2$; the corresponding *acid*; its *hydrochloride*; *copper* salt $(+1\frac{1}{2}H_2O)$; *methyl* ester, b. p. 193°/14 mm., D_4^{20} 1·0216, n_D^{20} 1·4533, and its *hydrochloride*, decomposing at 173° when heated rapidly in a sealed capillary, were prepared.

aa'-Pentamethylenedi-iminodiisobutyronitrile, $C_5H_{10}(NH\cdot CMe_2\cdot CN)_2$, forms colourless crystals, m. p. 46—47°; its *hydrochloride* was prepared. The *acid*, which is stable even at 360°, and its *hydrochloride*; the *methyl* ester, which forms a colourless liquid, b. p. 193°/14 mm., D_4^{20} 1·0035, n_D^{20} 1·4538, and its *hydrochloride* were prepared. The *copper* salt apparently exists in two modifications: an insoluble form, $C_{13}H_{24}O_4N_2Cu$, and a soluble acid salt, $C_{13}H_{26}O_4N_2 + 3C_{13}H_{24}O_4N_2Cu$.

T. H. P.

Crystallographic Study of the Cuprammonium Derivatives of Cyanomethyl- and Benzylcyanomethyl-glutaconimides. (Mlle.) Fausta Balzac (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 133—137).—The cuprammonium derivative of cyanomethylglutaconimide, $(C_7H_5O_2N_2)_2[Cu(NH_3)_4],2H_2O$ (compare Guareschi, A., 1898, i, 205) crystallises in the prismatic class of the monoclinic system; $[a:b:c = 1·3406:1:2·0107,\ \beta = 95°\ 59']$, D^{17} 1·539. The cuprammonium derivative of benzylcyanomethylglutaconimide (Guareschi, *loc. cit.*) crystallises in the triclinic system; $[a:b:c = 0·7941:1:?,\ a = 94°\ 42'\ 6'',\ \beta = 121°\ 51'\ 7'',\ \gamma = 69°\ 58'\ 15'']$, D^{23} 1·424.

Thus, the introduction of the benzyl group into the molcule of cyanomethylglutaconimide produces a complete change in the crystalline structure of the cuprammonium derivative; in addition, the intensity of the colour and the density diminish, whilst the molecular volume increases.

T. H. P.

Metallic Derivatives and Constitution of Guanidine. Hans Krall (T., 1915, **107**, 1396—1405; compare T., 1913, **103**, 1378).—Guanidine decomposes at 160° with evolution of ammonia and formation of melamine. In the presence of an equimolecular proportion of potassium ethoxide, decomposition occurs less readily, the residue at 200° consisting of potassium cyanamide, whilst that obtained with a bimolecular quantity of potassium ethoxide consists mainly of dipotassium cyanamide; judging by the probability that the potassium compounds of cyanamide are derived from the structure NH:C:NH, the suggestion is made that potassium derivatives of guanidine are intermediarily produced in which the metal replaces the hydrogen of an imino-radicle. When boiled in aqueous solution, guanidine undergoes hydrolysis with formation of ammonia and a little melamine; no indication of the formation of urea is observable. Nitrous acid acts but slowly on guanidine and the maximum amount of nitrogen liberated is equivalent to the destruction of only one amino-group. Guanidine does not form a dihydrochloride.

These results are held to discredit the structure $NH{:}C(NH)_2$ for guanidine, and it is suggested that guanidine in solution is a mixture of isomeric forms of the structures $\overset{NH_3}{\underset{N}{|}}\!\!>\!C\cdot NH_2$ and $\overset{NH_3}{\underset{NH}{|}}\!\!>\!C{:}NH$,

(analogous to the suggestion already made for thiocarbamide and carbamide; Werner, T., 1912, **101**, 2185; 1913, **103**, 1013). Acids are considered to increase the relative proportion of the first form and alkalis that of the latter.

The salt-formation of guanidine with metals is adduced in support of this view; guanidine gives a colourless *monosilver* derivative, possibly of the structure $\begin{matrix}NH_3\\|\\NAg\end{matrix}\!\!>\!C{:}NH$, an explosive black *disilver* derivative, possibly $\begin{matrix}NH_3\\|\\NAg\end{matrix}\!\!>\!C{:}NAg$, and a yellow derivative, probably identical with that described by Thiele (A., 1899, i, 7; also Schenck, A., 1910, i, 99) which appears to be a mixture of the two preceding compounds. There were also obtained a green *copper* derivative, possibly $\begin{matrix}NH_3\\|\\N\end{matrix}\!\!=\!\!>\!C{:}NCu$, and unstable blue needles of a *compound*, $C_2H_9N_6ClCu$. D. F. T.

Synthesis of Tetramethylenediguanidine. ALEXANDER KIZEL (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 898—908).—The action of an aqueous solution of cyanamide on tetramethylenediamine yields agmatine (compare Kossel, A., 1910, i, 500, 655), whereas, under similar conditions, pentamethylenediamine gives pentamethyldiguanidine (compare Ripke, A., 1911, i, 620). In such slow reactions as these, the low yields obtained may be due to polymerisation of the cyanamide. The author finds, indeed, that addition of the cyanamide in portions at intervals to the tetramethylenediamine (compare Schulze and Winterstein, A., 1902, i, 231) results in a much larger yield of agmatine than was obtained by Kossel, and in the simultaneous formation of tetramethylenediguanidine,

$$NH{:}C(NH_2)\cdot NH\cdot[CH_2]_4\cdot NH\cdot C(NH_2){:}NH,$$

or, less probably, $NH{:}C(NH_2)\cdot NH\cdot C(:NH)\cdot NH\cdot[CH_2]_4\cdot NH_2$. Thus, the action of cyanamide on tetramethylenediamine is similar to that on pentamethylenediamine, mono- and di-guanidine derivatives being formed in each case; in the former instance, the di-, and in the latter, the mono-derivative is formed in relatively small proportion. In view of the constitution of vitiatine, which occurs in Liebig's meat extract and in urine (compare Kutscher, A., 1907, ii, 568, 708), it seems possible that both tetra- and penta-methylenediguanidines play some part in the metabolism of organisms.

Tetramethylenediguanidine sulphate, $C_6H_{16}N_6,H_2SO_4$, forms spherical aggregates of blunt needles, m. p. 291° (uncorr.), and begins to blacken at 288—289°; one part of the salt dissolves in 156·5 parts of water at 21°. The *carbonate*; *hydrochloride*; *picrate*, $C_6H_{16}N_6,2C_6H_3O_7N_3$, m. p. 253—254°, which commences to darken at 239°; *picrolonate*, m. p. 278—279° (uncorr.) (decomp.); *aurichloride*, $C_6H_{16}N_6,2HAuCl_4$, m. p. 172·5° (uncorr.); and *platinichloride*, which darkens at 215°, m. p. 224° on rapid heating, were prepared.

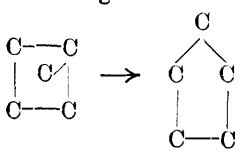
Tetramethylenediguanidine may be precipitated quantitatively by the method used by Kossel and Kutscher for arginine (A., 1901, i,

107), namely, addition of the requisite quantity of an aqueous solution of a silver salt and then excess of baryta. The base is also precipitated, more completely than arginine is, by phosphotungstic acid.

T. H. P.

A. Mayer's Experiments and the Phenomena of Isomerisation of Cyclic Compounds. N. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 831—835).—Mayer (*Phil. Mag.*, 1879, [v], **7**, 98) determined the equilibrium figures of groups of movable magnets under the influence of a fixed magnetic pole. With more than four floating magnets, the latter are capable of different groupings varying in stability. Thus, five magnets give two configurations: (1) four arranged at the angles of a square and the fifth one central; this represents the unstable isomeric form, a slight shake of the containing vessel being sufficient to convert it into (2) the stable pentagonal form. With six magnets, the unstable form is hexagonal and passes easily into the stable arrangement, which is pentagonal with a central magnet. With seven magnets, the stable form is hexagonal with a central magnet. With eight magnets, the unstable heptagonal arrangement, with one magnet in the centre, changes readily into the stable hexagonal form, with two central magnets. The stabilities of these systems, as described above, refer only to the case when the whole system is at rest, and when this condition is not satisfied, the stability may undergo change. For instance, the unstable ring of six magnets becomes stable under the influence of a sufficiently rapid rotation.

Analogies are drawn between the above results and the phenomena of isomerisation in cyclic compounds, the following cases being cited: conversion of (1) derivatives of *cyclo*butane into derivatives of *cyclo*pentane (annexed formula); (2) *cyclo*hexane compounds into *cyclo*pentane derivatives; (3) derivatives of *cyclo*heptane into those of *cyclo*hexane. In some cases, however, the isomerisation of cyclic compounds does not proceed in the derivatives corresponding with these schemes, derivatives of *cyclo*pentane, for instance, being capable of passing into *cyclo*hexane compounds. For such conversion, Mayer's results show the necessary condition to be rotation of the whole system, this rendering the hexagonal arrangement stable. In his development of the corpuscular theory of atomic structure, Thomson arrived theoretically at results similar to those of Mayer's experiments with magnets. Thus, one and the same mechanical model serves for illustrating the structures of atoms and molecules. T. H. P.



Hydroaromatic Compounds with *gem*-Dialkyl Groups. K. VON AUWERS and E. LANGE (*Annalen*, 1915, **409**, 149—182).—The authors have continued their previous work (A., 1914, i, 50), but the complete description of the results, dealing with the relation between the constitution and the physical constants of substances with and without *gem*-dialkyl groups, will be published later when some of the compounds have been more carefully purified.

1-*Methyl*-1-*dichloromethyl*cyclo*hexane*, $C_6H_{10}Me\cdot CHCl_2$, prepared from the corresponding *cyclo*hexan-4-one by Zelinsky's method with zinc and palladium and alcoholic hydrogen chloride, has b. p. 99°/18 mm., D_4^{20} 1·131, n_α 1·48670, n_D 1·48947, n_β 1·49596, and n_γ 1·50145. 1 : 1-*Dimethyl*-Δ^3-cyclo*hexene*, prepared from 1 : 1-dimethyl*cyclo*hexan-4-ol (*loc. cit.*) and phosphoric oxide, has b. p. 120—122°/750 mm., D_4^{20} 0·804, n_α 1·44604, n_D 1·44849, n_β 1·45531, and n_γ 1·46100, and yields $\beta\beta$-dimethyladipic acid by oxidation in acetone with potassium permanganate, or, better, in glacial acetic acid with ozone; in the latter method, the dialdehyde of $\beta\beta$-dimethyladipic acid is also obtained. 1 : 1 : 4-*Trimethyl*-Δ^3-cyclo*hexene*, b. p. 36·3—37·3°/14 mm., $D_4^{23\cdot15}$ 0·8021, n_α 1·44152, n_D 1·44422, n_β 1·45086, n_γ 1·45652 at 23·15°, is best prepared by heating 1 : 1 : 4-trimethyl*cyclo*hexan-4-ol with anhydrous oxalic acid at 140° in a current of carbon dioxide. It forms a *nitrosochloride*, $C_9H_{16}ONCl$, stout rhombohedra or needles, m. p. 118—122°, and *dibromide*, b. p. 120—120·5°/10 mm; the *hydrobromide*, $C_9H_{17}Br$, colourless prisms, m. p. 27—28°, b. p. 77—79°/17—18 mm., can only be obtained from the trimethyl*cyclo*hexanol by the action of hydrogen bromide in glacial acetic acid. The oxidation of the trimethyl*cyclo*hexene by ozone in glacial acetic acid at 0° yields an unsaturated ketone (isolated in the form of the *semicarbazone*, $C_{10}H_{17}ON_3$, colourless needles, m. p. 217°) and an acid, which is probably ϵ-*keto*-$\beta\beta$-*dimethylheptoic acid*, $COMe\cdot CH_2\cdot CH_2\cdot CMe_2\cdot CH_2\cdot CO_2H$, b. p. 178°/17 mm., $D_4^{14\cdot7}$ 1·0370, n_α 1·45646, n_D 1·45894, n_β 1·46516 at 14·7°, the *semicarbazone* of which, colourless needles and leaflets, m. p. 156—158°, is soluble in alkalis.

1 : 4-*Dimethyl*-1-*dichloromethyl*-Δ^3-cyclo*hexene*,

$$CHCl_2\cdot CMe\begin{matrix}<\\>\end{matrix}\begin{matrix}CH_2\cdot CH_2\\CH_2-CH\end{matrix}\begin{matrix}>\\=\end{matrix}CH,$$

b. p. 110—110·5°/16 mm., D_4^{23} 1·1227, n_α 1·49622, n_D 1·49913, n_β 1·50650, n_γ 1·51275 at 23°, is prepared by heating the corresponding tertiary alcohol with 98% formic acid on the water-bath. When 1 : 1 : 2-trimethyl*cyclo*hexan-2-ol (*loc. cit.*) is heated with anhydrous oxalic acid in a current of carbon dioxide it yields 1 : 1 : 2-*trimethyl*-Δ^2-cyclo*hexene*, b. p. 147·2-150°/740 mm., $D_4^{20\cdot3}$ 0·8217, n_α 1·45336, n_D 1·45603, n_β 1·46298, n_γ 1·46877 at 20·4°, which forms a *nitrosochloride*, pearly needles, m. p. 133—134°, and yields by oxidation with cold 2% potassium permanganate a ketonic acid (Crossley and Renouf's ϵ-keto-$\delta\delta$-dimethylheptoic acid?), the semicarbazone of which has m. p. 167—169°.

1 : 4 : 4-Trimethyl-1-dichloromethyl*cyclo*hexan-2-one has m. p. 74° and b. p. 137—137·5°/17 mm. (compare Auwers and Hessenland, A., 1908, i, 550) and is reduced by sodium and moist ether, with the subsequent careful addition of water, to 1 : 1 : 4 : 4-*tetramethyl*cyclo*hexan*-2-*ol*, colourless prisms, m. p. 53°, softening at 51°, b. p. 201·5—203°/745 mm., $D_4^{31\cdot1}$ 0·8915, n_α 1·45431, n_D 1·45665, n_β 1·46256, n_γ 1·46727 at 31·4°. The *cyclo*hexanol is oxidised by dilute sulphuric acid and potassium dichromate to 1 : 1 : 4 : 4-*tetramethyl*cyclo*hexan*-2-*one*, b. p. 190·4° or 77°/16 mm., $D_4^{14\cdot4}$ 0·8930, n_α 1·44635, n_D 1·44849, n_β 1·45452, n_γ 1·45957 (*semicarbazone*, colourless crystalline powder, m. p. 202—204°).

1-*Methyl*-1-*dichloromethyl*-4 : 4-*diethyl*cyclo*hexan*-2-*one*, prepared from 1-methyl-1-dichloromethyl-4-ethyl-Δ^3-*cyclo*hexen-2-one and magnesium ethyl iodide in the usual manner, forms glistening prisms, m. p. 65°, b. p. 168—172°/20 mm., and is reduced by sodium and moist ether to 1 : 1-*dimethyl*-4 : 4-*diethyl*cyclo*hexan*-2-*ol*, which has an odour of camphor, b. p. 117—118°/11 mm., $D_4^{13\cdot9}$ 0·9194, n_α 1·47367, n_D 1·47588, n_β 1·48213, n_γ 1·48715 at 13·6°. The alcohol by oxidation yields 1 : 1-*dimethyl*-4 : 4-*diethyl*cyclo*hexan*-2-*one*, b. p. 233—235°/742 mm., or 103-104°/10 mm., D_4^{15} 0·9114, n_α 1·46086, n_D 1·46307, n_β 1·46914, n_γ 1·47419 at 15·2°, which forms a *semicarbazone*, $C_{13}H_{25}ON_3$, colourless needles, m. p. 157—158°. C. S.

Mixtures of Nitrated Explosives and Nitration of Toluene. Michele Giua (*Gazzetta*, 1915, **45**, ii, 32—44).—The author has investigated the solidification diagrams of the following systems: 2 : 4 : 6-Trinitrotoluene—2 : 4 : 6-trinitromethylnitroaniline forms an additive compound, $3C_6H_2Me(NO_2)_3,2NO_2{\cdot}NMe{\cdot}C_6H_2(NO_2)_3$, which dissociates on fusion. *p*-Nitrotoluene—2 : 4 : 6-trinitromethylnitroaniline forms an eutectic with two closely adjacent solidification points. 2 : 4 : 6-Trinitrotoluene—hexanitrodiphenylamine forms solid solutions, all the mixtures having intense canary-yellow colours.

The yields of 2 : 4-dinitrotoluene obtained on nitrating toluene with nitrating mixtures of different compositions have been studied, as also has the time-temperature diagram of the nitration. T. H. P.

Precipitation of Trinitrotoluene from Concentrated Acid Solution by Means of Water. W. McHutchison and R. Wright (*J. Soc. Chem. Ind.*, 1915, **34**, 781—782).—Experiments have been conducted with the object of determining the minimum quantity of water which is required to precipitate trinitrotoluene completely from its acid mother liquor. Three solutions were examined, one being a saturated solution of the crude explosive in a mixture containing 80% of sulphuric acid, 10% of nitric acid, and 10% of water, another being an unsaturated solution in the same mixture, whilst the third was an actual sample of "residue acid" obtained from the factory (H_2SO_4, 86·3%; HNO_3 6·71%; HNO_2, 0·5%; water, etc., forming the difference).

It is found that the maximum recovery of the dissolved explosive is obtained by the addition of four or five volumes of water, or, in the case of the above technical sample, sufficent to lower the density from 1·850 to about 1·2. The addition of more water not only renders the re-concentration of the acid unduly expensive, but actually causes a decrease in the amount of precipitate. J. C. W.

Metallic Salts of Ammono-Acids [Acid Amides]. Edward C. Franklin (*Proc. Nat. Acad. Sci.*, 1915, **1**, 68—70).—Some more reactions in liquid ammonia are described.

I. Just as "ammono-acids," that is, acid-amides, react with potassium amides in liquid ammonia (A., 1902, i, 748), so they dissolve insoluble metallic amides, imides, or nitrides to form salts. Thus, silver amide, prepared by mixing liquid ammonia solutions of silver nitrate and potassamide, dissolves in a liquid ammonia solution of benzene-

sulphonamide to form *silver benzenesulphonamide*, $SO_2Ph\cdot NHAg,2NH_3$. This crystallises well from concentrated solutions, and loses $1NH_3$ at 20° in a vacuum and the other at 200°. In a similar manner, the following salts have been prepared: *thallous benzenesulphonamide*, $SO_2Ph\cdot NHTl$, and with 1 and $2NH_3$, *thallous* p-*toluenesulphonamide*, $C_6H_4Me\cdot SO_2\cdot NHTl$, and with $2NH_3$, *thallous acetamide*, $CH_3\cdot CO\cdot NHTl$, and with $2NH_3$, *cuprous benzenesulphonamide* and p-*toluenesulphonamide*, both without and with $2NH_3$, and *silver acetamide*, also without and with $2NH_3$.

II. Cupric hydroxide and silver oxide dissolve in liquid ammonia solutions of benzenesulphonamide to form *cupric benzenesulphonamide*, $(SO_2Ph\cdot NH)_2Cu,4NH_3$, and the above silver benzenesulphonamide.

III. Alkyl and aryl derivatives of acid amides can be regarded as acid esters of the "ammono-acids." The remaining hydrogen should therefore be replaceable by a metal, by interaction with a metallic amide in liquid ammonia. This is the case, and *silver acetanilide*, $CH_3\cdot CO\cdot NPhAg$, also with $1NH_3$, has been obtained by the action of a solution of acetanilide on silver amide; *thallous acetanilide*, $CH_3\cdot CO\cdot NPhTl$, from thallous nitride; *potassium acetobenzylamide*, $CH_3\cdot CO\cdot N(CH_2Ph)K,NH_3$, from acetobenzylamide and potassium amide; and *potassium aceto*-p-*phenetidide*, $CH_3\cdot CO\cdot NK\cdot C_6H_4\cdot OEt$, from aceto-*p*-phenetidide. J. C. W.

Tolyl Esters and Toluidides of the Nitrosulphonic Acids of *p*-Xylene. Ralph C. Huston (*J. Amer. Chem. Soc.*, 1915, **37**, 2119—2122).—Karslake and Huston (A., 1914, i, 821) have described three nitro-*p*-xylene-2-sulphonic acids and some of their derivatives. An account is now given of the tolyl esters and toluidides of these acids.

The following derivatives of 6-nitro-*p*-xylene-2-sulphonic acid are described. The o-*tolyl ester*, m. p. 66—67° (corr.), opaque, flat, pointed crystals; the m-*tolyl ester*, m. p. 71·5—72° (corr.), rhombohedral plates; the p-*tolyl ester*, m. p. 93·5—94·5° (corr.), thin, lustrous plates; the o-*toluidide*, m. p. 126·5—127·5° (corr.), flat, slender needles; the p-*toluidide*, m. p. 135—136° (corr.), long, silky filaments.

3-Nitro-*p*-xylene-2-sulphonic acid furnishes the following derivatives: the o-*tolyl ester*, m. p. 151·5—152° (corr.), hard, opaque prisms; the m-*tolyl ester*, m. p. 107·5—108° (corr.), lustrous plates; the p-*tolyl ester*, m. p. 76—77° (corr.), needle-like plates; the o-*toluidide*, m. p. 143·5—145° (corr.), lustrous, rhombohedral plates; the p-*toluidide*, m. p. 158·5—159° (corr.), long, flat, lustrous needles.

The following compounds were obtained from 5-nitro-*p*-xylene-2-sulphonic acid. The o-*tolyl ester*, m. p. 99—100° (corr.), soft, flat, opaque needles; the m-*tolyl ester*, m. p. 110—111° (corr.), flat, lustrous needles; the p-*tolyl ester*, m. p. 117·5—118·5° (corr.), lustrous, needle-like plates; the o-*toluidide*, m. p. 140·5—141° (corr.), lustrous, faintly yellow plates; the p-*toluidide*, m. p. 143·5—144·5° (corr.), long, lustrous plates.

It is pointed out that the m. p.'s of the tolyl esters of the 5- and 6-nitro-*p*-xylene-2-sulphonic acids increase in the order *o*-, *m*-, *p*-, whereas those of the tolyl esters of the 3-nitro-acid decrease in the

same order. The *p*-toluidide of each acid has a higher m. p. than that of the *o*-toluidide. The solubility of the derivatives of each acid in organic solvents decreases as the m. p. increases. As a rule, the derivatives of the 5-nitro-acid are less soluble than those of the other two acids. E. G.

1 : 2-Diphenyl*cyclo*propane from Benzylideneacetophenone [Phenyl Styryl Ketone]. N. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1102—1111).—Like mesityl oxide, cinnamaldehyde, and styryl methyl ketone, phenyl styryl ketone contains the grouping C:CH·CO·, and reacts with hydrazine with formation of 3 : 5-diphenylpyrazoline, $CH_2<\begin{matrix}CPh=N\\ |\\ CHPh\cdot NH\end{matrix}$, which is capable of undergoing catalytic decomposition, nitrogen being liberated and 1 : 2-diphenyl*cyclo*propane formed.

3 : 5-*Diphenylpyrazoline*, $C_{15}H_{14}N_2$, forms rectangular plates or acicular crystals, m. p. 88°, and like other pyrazoline bases, is readily oxidised in the air. Its *hydrochloride*, $C_{15}H_{14}N_2,HCl$, m. p. 220—221° (decomp.) and *nitroso*-derivative, $CH_2<\begin{matrix}CPh=N\\ |\\ CHPh\cdot N\cdot NO\end{matrix}$, golden-yellow needles, m. p. 140° (decomp.), were prepared.

1 : 2-*Diphenyl*cyclo*propane*, $CH_2<\begin{matrix}CHPh\\ |\\ CHPh\end{matrix}$, prepared by heating 3 : 5-diphenylpyrazoline with solid potassium hydroxide and platinised porous tile, is a liquid, b. p. 307·5°/741 mm., 149°/9·5 mm., D_4^{20} 1·0317, n_D^{20} 1·5967, and remains unchanged when boiled in alcoholic solution with sulphuric acid, but combines with bromine, giving the compound CHPhBr·CH_2·CHPhBr. With hydrogen bromide it combines in two ways, giving: (1) *γ-bromo-βγ-diphenylpropane*, CHMePh·CHPhBr, which is a liquid and yields α-methylstilbene when treated with potassium hydroxide, and (2) *α-bromo-βγ-diphenylpropane*, $CH_2Br\cdot CHPh\cdot CH_2Ph$, which forms oblique, elongated, quadrilateral plates, m. p. 161—161·5° (decomp.), and gives βγ-diphenylpropylene when decomposed by potassium hydroxide. α-Methylstilbene may be partly converted into βγ-diphenylpropylene, and the latter into the former, by combination with hydrogen bromide and decomposition of the bromo-compound obtained by means of potassium hydroxide; the two transformations are represented by the schemes: (1) $CH_2{:}CPh\cdot CH_2Ph + HBr \longrightarrow CMePhBr\cdot CH_2Ph \longrightarrow HBr + CMePh{:}CHPh$, and (2) $CMePh{:}CHPh + HBr \longrightarrow CMePhBr\cdot CH_2Ph \longrightarrow CH_2Br\cdot CHPh\cdot CH_2Ph \longrightarrow CH_2{:}CPh\cdot CH_2Ph + HBr$.

T. H. P.

Action of Trioxymethylene on *p*-Xylene in Presence of Aluminium Chloride. RALPH C. HUSTON and DWIGHT T. EWING (*J. Amer. Chem. Soc.*, 1915, **37**, 2394—2399).—Frankforter and Kokatnur (A., 1914, i, 1060) have stated that the action of trioxymethylene on benzene, toluene, *o*-xylene, and mesitylene in presence of aluminium chloride proceeds in accordance with the

equation, $4C_6H_6 + (CH_2O)_3 = CH_2Ph_2 + C_{14}H_{10} + 3H_2O + H_2$. A study has now been made of the behaviour of *p*-xylene with trioxymethylene and aluminium chloride under similar conditions. The results do not conform with those to be anticipated from Frankforter and Kokatnur's equation, but show that in the case of *p*-xylene the derivatives of diphenylmethane and anthracene are not formed in equimolecular quantities. It is pointed out that the molecular weights of the compounds obtained by Frankforter and Kokatnur were not determined by them.

The following compounds were produced in the reaction with *p*-xylene. *Methylenebisdi*-p-*xylylmethane*, $CH_2(C_6H_2Me_2 \cdot CH_2 \cdot C_6H_3Me_2)_2$, m. p. 204—205° (decomp.), is a yellowish-brown powder. *Di*-p-*xylylmethane*, $CH_2(C_6H_3Me_2)_2$, m. p. 60—60·5°, crystallises in long, white needles. A third *compound*, possibly *p*-xylylmethyldi-*p*-xylylmethane, m. p. 157—158°, forms colourless crystals.

The results of this work afford evidence that trioxymethylene is dissociated into formaldehyde under the conditions of the experiments and that the latter is the active agent in the condensation reactions. E. G.

Action of Trioxymethylene on Various Hydrocarbons in the Presence of Aluminium Chloride. G. B. Frankforter and V. Kokatnur (*J. Amer. Chem. Soc.*, 1915, **37**, 2399—2401).—A reply to the criticisms of Huston and Ewing (preceding abstract) on the authors' work on the action of trioxymethylene on benzene hydrocarbons in presence of aluminium chloride (A., 1914, i, 1060). E. G.

Action of Trioxymethylene on *p*-Xylene in the Presence of Aluminium Chloride. II. Ralph C. Huston and Dwight T. Ewing (*J. Amer. Chem. Soc.*, 1915, **37**, 2401).—A reply to Frankforter and Kokatnur (preceding abstract). E. G.

Condensation of Derivatives of Di-α-naphthylmethane with Phenol and Aniline. O. Ju. Magidson (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1302—1310).—By condensing di-α-naphthylcarbinol with phenol in glacial acetic acid solution, Schmidlin and Massini (A., 1909, i, 561, 563) obtained a compound which they regarded as the phenyl ether of di-α-naphthylcarbinol. The author finds that the interaction of di-α-naphthylbromomethane and phenol yields a compound identical in properties with that obtained by Schmidlin and Massini; with concentrated sulphuric acid, however, it gives slowly a cherry-red coloration and not instantly the greenish-blue coloration characteristic for di-α-naphthylcarbinol and its ethers, and hydrogen bromide in glacial acetic acid solution is without action on it either in the cold or when heated in a sealed tube. The compound proves to be *p*-hydroxyphenyl-α-naphthylmethane; with alcoholic potassium hydroxide it readily forms the corresponding phenoxide, which is easily convertible into the methoxy-compound by the action of methyl sulphate.

From di-α-naphthylcarbinol and aniline, Schmidlin and Massini (*loc. cit.*) obtained a compound, $C_{27}H_{21}ON$, the oxygen being estimated

by difference. The author shows that this compound, which is also obtainable by condensation of di-α-naphthylbromomethane and aniline, is *p*-aminophenyldi-α-naphthylmethane mixed with a certain proportion of its hydrochloride, the hydrogen chloride being only incompletely removed by crystallisation from acetic acid solution. The free base and certain of its salts have been prepared and analysed.

p-*Hydroxyphenyldi-α-naphthylmethane*, $OH\cdot C_6H_4\cdot CH(C_{10}H_7)_2$, forms shining, white crystals, m. p. 213—215°; Schmidlin and Massini found m. p. 212—214°. The *potassium* derivative forms thin, silky leaflets, darkening and softening at about 235°, m. p. 245—255° (charring).

p-*Anisyldi-α-naphthylmethane*, $OMe\cdot C_6H_4\cdot CH(C_{10}H_7)_2$, forms a fine, crystalline powder, m. p. 187—190.°

p-*Aminophenyldi-α-naphthylmethane*, $NH_2\cdot C_6H_4\cdot CH(C_{10}H_7)_2$, forms crystals, m. p. 225—226° or 222—224°. Its *sulphate*, $C_{27}H_{21}N,H_2SO_4$, m. p. about 325° (decomp.) and its *hydrochloride*, $C_{27}H_{21}N,HCl$, m. p. 210—214°, were prepared. Replacement of the amino-group of the base by hydroxyl by means of the diazo-reaction results in the formation of *p*-hydroxyphenyldi-α-naphthylmethane (*vide supra*).

T. H. P.

Action of Benzoic Acid on Dimethylaniline. KARL NEUNDLINGER (*Annalen*, 1915, **409**, 182—187).—Repeating Fischer's work in 1881 on the reaction between benzoic acid and dimethylaniline, the author has heated the two substances together at 220° with the gradual addition of phosphoric oxide. The product is shown to be a mixture containing *p*-dimethylaminobenzophenone, benzoylmonomethylanilide, and tetramethyldiaminodiphenylmethane. C. S.

Action of Diphenylcarbamyl Chloride on Organic Bases. WILLIAM M. DEHN and EARL M. PLATT (*J. Amer. Chem. Soc.*, 1915, **37**, 2122—2130).—In earlier papers (Dehn, A., 1912, i, 833; Dehn and Bell, A., 1914, i, 1169) an account has been given of the action of acetyl chloride and benzoyl chloride on organic bases dissolved in dry ether. A study has now been made of the action of diphenylcarbamyl chloride under these conditions. The results show that this substance is less reactive than acetyl and benzoyl chlorides, but the action can be promoted by sunlight or heat with formation of additive compounds or their dissociation products. It is shown that these reactions are not ionic in character.

Diphenylcarbamyl chloride unites with piperidine to form diphenylpiperidylcarbamide hydrochloride, but this compound cannot be obtained by the addition of hydrogen chloride to diphenylpiperidylcarbamide. The reaction between diphenylcarbamyl chloride and the toluidines is rapid in the case of the para-compound, much slower in the case of the meta-compound, and in the case of the ortho-compound only traces of a product are formed after five months' exposure to sunlight. This phenomenon is discussed as a case of steric hindrance.

Diphenyl-p-*tolylcarbamide*, $NPh_2\cdot CO\cdot NH\cdot C_6H_4Me$, m. p. 130°, forms prismatic needles, and *diphenyl*-m-*tolylcarbamide*, m. p. 125—126°, rhombic plates; *diphenyl*-o-*tolylcarbamide*, m. p. 119°, obtained by

heating the reaction mixture at 115° in a sealed tube, crystallises in rectangular plates or tufts of needles. Diphenylcarbamyl chloride reacts with phenylhydrazine with formation of *aδδ-triphenylsemicarbazide*, $NHPh\cdot NH\cdot CO\cdot NPh_2$, m. p. 149—150°, which crystallises in rhombic plates. *Diphenylpiperidylcarbamide*, m. p. 122°, forms hexagonal and rhomboidal plates.

Diphenylcarbamyl chloride has also been found to react with the following bases, but the products have not yet been fully investigated: *p*-tolylhydrazine, *as*-diphenylhydrazine, *as*-phenylbenzylhydrazine, α-naphthylamine, benzidine, *p*-aminophenol, *o*-chloroaniline, *p*-bromoaniline, *p*-anisidine, *iso*butylamine, hexylamine, heptylamine, di*iso*butylamine, di*iso*amylamine, diphenylamine, quinoline, pyridine, picoline, triethylamine, tri*iso*butylamine, tri*iso*amylamine, diethylaniline, and tribenzylamine. E. G.

Molecular Rearrangements of Triphenylmethane Derivatives. I. and II. JULIUS STIEGLITZ (*Proc. Nat. Acad. Sci.*, 1915, **1**, 196—202, 202—210).—I. *General discussion.* Several examples of molecular rearrangements are interpreted in terms of Thomson's electron theory of valences.

II. *Experimental part.* A. *Molecular Rearrangements of Triphenylmethyl Halogenoamines.* [With ISABELLE VOSBURGH and AGNES FAY MORGAN]. (Compare A., 1913, i, 852). A rearrangement into phenyliminobenzophenones has been established in the case of triphenylmethylbromoamine, phenyldi-*p*-chlorophenylmethylchloroamine (the products being identified by their hydrolysis into *pp'*-dichlorobenzophenone and aniline, and *p*-chlorobenzophenone and *p*-chloroaniline), phenylchlorophenylbromophenylmethylchloroamine, triphenylmethyldichloroamine, and diphenylchlorophenylmethyldichloroamine, $C_6H_4Cl\cdot CPh_2\cdot NCl_2$. Triphenylmethylchloromethylamine, $CPh_3\cdot NMe\cdot Cl$, on the other hand, could not be rearranged. These reactions are conditioned by the positive halogen atom which tends to go over into its stable negative form. If it can secure the necessary two electrons from the nitrogen atom, as in the former cases, it does so, and thus leaves the nitrogen incapable of holding the H^+ and the Cl^-, which are therefore eliminated. A univalent nitrogen atom is consequently exposed and the subsequent rearrangements are possible.

B. *Molecular Rearrangement of β-Triphenylmethyl-β-methylhydroxylamine.* [With BERT ALLEN STAGNER.] (Compare Stieglitz and Leech, A., 1914, i, 268). This base, when treated with phosphorus pentachloride in ethereal solution, undergoes normal rearrangement, the product yielding methylaniline and benzophenone on hydrolysis, thus,

$$CPh_3\cdot NMe\cdot OH \longrightarrow CPh_2Cl\cdot NMePh \xrightarrow{+H_2O} COPh_2 + C_6H_5\cdot NHMe,HCl.$$

Diphenylchlorophenylmethylmethylhydroxylamine,

$$C_6H_4Cl\cdot CPh_2\cdot NMe\cdot OH,$$

behaves in the same way. Thus, for the first time, it is shown that substances which cannot form univalent nitrogen derivatives can also suffer the same rearrangement. How this may be is uncertain, but the first condition is the tendency of the positive hydroxyl group to change into a negative group.

C. *Rearrangement of Triphenylmethyl Azoimides and of* s-*Di-triphenylmethylhydrazine.* [With JAMES KUHN SENIOR.] When triphenylmethyl azoimide is heated, it loses nitrogen and then changes into benzophenoneanil, thus, $CPh_3 \cdot N_3 \rightarrow CPh_2 \cdot NPh + N_2$. In this case there can be no question of a direct exchange of radicles as postulated by Beckmann. That the intervention of a compound with univalent nitrogen can account for the rearrangement is also seen in the following case. Diphenylchlorophenylmethylazoimide,

$$C_6H_4Cl \cdot CPh_2 \cdot N_3,$$

should give the same univalent nitrogen compound, $C_6H_4Cl \cdot CPh_2 \cdot N:$, as the hydroxylamine, $C_6H_4Cl \cdot CPh_2 \cdot NH \cdot OH$, and, therefore, the ratio of the products of rearrangement, $CPh_2 \cdot N \cdot C_6H_4Cl$ and

$$C_6H_4Cl \cdot CPh \cdot NPh,$$

should be the same. This was tested by titrating the anilines formed on hydrolysis of these products, and it was found that the ratio of aniline to chloroaniline was 70 : 30 in the case of the azoimide and 71 : 29 in the case of the hydroxylamine.

It was also expected that triphenylmethylhydrazine would lose ammonia and thus be exposed to the same possibility of rearrangement, thus, $CPh_3 \cdot NH \cdot NH_2 \rightarrow CPh_2 \cdot NPh + NH_3$, but this could not be proved. It is recognised that this is due to ignorance of the electronic structure of the hydrazines. There can be no doubt about the electronic structure of di-triphenylmethylhydrazine,

$$CPh_3 \cdot NH \cdot NH \cdot CPh_3,$$

however, which would leave a univalent nitrogen derivative in whatever way it lost triphenylmethylamine. When heated with zinc chloride, it does indeed give a product which yields aniline on hydrolysis, although the other compounds have not yet been identified.

J. C. W.

Action of Selenium Bromide on Magnesium Bromide Derivatives. II. A. PIERONI and G. BALDUZZI (*Gazzetta*, 1915, **45**, ii, 106—111. Compare A., 1914, i, 1198).—Selenium bromide reacts readily with magnesium phenyl bromide and with magnesium *m*-aminophenyl bromide, the reaction in the former case being expressed by the following equations: $2MgPhBr + Se_2Br_2 = 2MgBr + SePh \cdot SePh$; $Se_2Ph_2 = Se + SePh_2$; $SePh_2 + Br_2 = SePh_2Br_2$ (compare Krafft and Lyons, A., 1894, i, 448). In the latter case similar changes occur.

m-*Aminophenyl selenide*, $NH_2 \cdot C_6H_4 \cdot Se \cdot C_6H_4 \cdot NH_2$, forms a yellowish-brown, heavy, viscous oil, b. p. 130—150°/vac. When treated in ethereal solution with bromine, it yields the *compound*,

$$Se(C_6H_3Br \cdot NH_2, HBr)_2,$$

which crystallises in tufts of white needles, m. p. 115—116°.

T. H. P.

Transformation of Trinitrotoluene into Trinitrophenylethanol [Trinitrobenzylcarbinol]. VEZIO VENDER (*Gazzetta*, 1915, **45**, ii, 97—99).—The conversion of nitrotoluenes into stilbene derivatives by the action of aromatic aldehydes is regarded as a general reaction for aldehydes. With formaldehyde, however, the author finds

that derivatives of benzylcarbinol are formed. Thus, formaldehyde and 2 : 4 : 6-trinitrotoluene yield the corresponding trinitrobenzylcarbinol. Acetaldehyde readily undergoes a similar condensation, but the product formed, which is being investigated, exhibits no alcoholic function.

2 : 4 : 6-*Trinitrobenzylcarbinol*, $OH\cdot CH_2\cdot CH_2\cdot C_6H_2(NO_2)_3$, formed from 2 : 4 : 6-trinitrotoluene and formaldehyde in presence of sodium hydroxide or potassium hydrogen carbonate, forms pale, yellow needles, or large, hard, crystals, m. p. 112°, with a characteristic sweet-bitter taste. The *acetate*, $OAc\cdot CH_2\cdot CH_2\cdot C_6H_2(NO_2)_3$, forms flat, lemon-yellow needles, m. p. 98°, and the *nitrate*,

$$NO_2\cdot O\cdot CH_2\cdot CH_2\cdot C_6H_2(NO_2)_3,$$

lemon-yellow crystals, m. p. 83°, which turn brown in the light.

T. H. P.

Formation of Simple and Mixed Ethers in the Action of Certain Magnesium Alkyl Iodides on Esters. G. L. Stadnikov (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1122—1125).—The author has previously (A., 1914, i, 954; this vol., i, 372) observed the formation of dibenzhydryl ether by the action of benzhydryl acetate on magnesium haloids. It is now suggested that this ether is formed in accordance with the equation, $CHPh_2\cdot O\cdot MgI + CHPh_2I = CHPh_2\cdot O\cdot CHPh_2 + MgI_2$, the benzhydryl iodide being obtained by the action of magnesium iodide on benzhydrylacetate, $CH_3\cdot CO_2\cdot CHPh_2 + MgI_2 = CH_3\cdot CO_2\cdot MgI + CHPh_2I$. Magnesium iodide is always present in Grignard's solution, and as it is continually regenerated during the further action of the iodide with the alcoholate, the presence of a small proportion of this salt is sufficient to convert a considerable quantity of ester into ether. Since the formation of iodide from the ester of an alcohol of high molecular weight may take place at a high temperature, it is to be expected that the action of ethyl acetate on the iodomagnesium alcoholate of benzhydrol, giving benzhydryl acetate at the ordinary temperature, would give an ether at a higher temperature; on the other hand, owing to the formation in the first phase of the reaction of benzhydryl acetate and the consequent presence of iodomagnesium ethoxide, the formation of two ethers, namely, dibenzhydryl ether and benzhydryl ethyl ether, should take place. The fact that these two ethers are actually obtained confirms the explanation of their formation given above.

T. H. P.

Preparation of a Substance Similar to Scymnolsulphuric Acid. Cholesterylsulphuric Acid. John A. Mandel and Carl Neuberg (*Biochem. Zeitsch.*, 1915, **71**, 186—195. Compare Hammarsten A., 1898, ii, 711).—Cholesterol, in the presence of chloroform and pyridine, readily yields on treatment with chlorosulphonic acid, cholesteryl sulphuric acid, according to the equation $C_{27}H_{45}\cdot OH + Cl\cdot SO_3H = HCl + C_{27}H_{44}\cdot O\cdot SO_3H$. After distillation of the solvents and treatment of the residue with the corresponding alkalis, the potassium, sodium, and ammonium salts could be obtained. These are only sparingly soluble in water, but they can be recrystalised from 80% alcohol, from which they separate in the first instance as a gel,

which gradually changes into crystals. The potassium salt has m. p. 235° and the ammonium salt m. p. 185°. On treatment with glacial acetic acid, the potassium salt yields acetylcholesterol and potassium hydrogen sulphate, and by treatment with hydrochloric acid, it yields cholesterol and sulphuric acid. Suspensions of the salt give colour reactions similar to those given by cholesterol. S. B. S.

Normal Ammonium Salts of Some Substituted Benzoic Acids. V. LEROY MCMASTER and I. H. GODLOVE (*J. Amer. Chem. Soc.*, 1915, **37**, 2181—2188).—In earlier papers (Keiser and McMaster, A., 1913, i, 248; McMaster, A., 1913, i, 444; 1914, i, 481, 1122) an account has been given of the preparation of the normal ammonium salts of various organic acids by passing dry ammonia into solutions of the acids in organic solvents. In continuation of this work, the authors have prepared ammonium m-*toluate*, *p*-toluate, *o*-, *m*-, and *p*-chlorobenzoates, o-*bromobenzoate*, m-*bromobenzoate*, *p*-bromobenzoate, *o*-, *m*-, and *p*-nitrobenzoates, 3 : 5-dinitrobenzoate, and *o*-, *m*-, and p-*aminobenzoates*.

Ammonium 3 : 5-diaminobenzoate could not be prepared by this method owing to the great solubility of the salt in organic liquids.

E. G.

Some Nitro-derivatives of *o*-Toluic Acid. MAX MAYER (*J. pr. Chem.*, 1915, [ii], **92**, 137—173).—The 3- and 5-nitro-*o*-toluidines have been converted, through the Sandmeyer reaction, into nitriles and then into the 3- and 5-nitro-*o*-toluic acids, and a number of derivatives of these have been prepared.

A suspension of finely-divided 5-nitro-*o*-toluidine hydrochloride was diazotised and the solution was added to a solution of copper sulphate and potassium cyanide at 70°, when the nitrile was precipitated. This was freed from inorganic material by sublimation, and 5-*nitro*-o-*toluonitrile*, $NO_2 \cdot C_6H_3Me \cdot CN$, was thus obtained in long, glistening, yellow, felted needles, m. p. 113—115°. The nitrile was hydrolysed by boiling concentrated sodium hydroxide to 5-*nitro*-o-*toluic acid*, m. p. 151°, which is identical with the "γ-nitrotoluic acid" obtained by oxidising 4-nitro-*o*-xylene.

All attempts to reduce the nitrile to 5-amino-*o*-toluonitrile failed, an experience which Beilstein and Kreusler met with in the case of the isomeric 6-nitro-*m*-toluonitrile (*Annalen*, 1867, **144**, 175). This is apparently due to the combined influence of the para-cyano-group and the alkyl group on the stability of the nitro-group, for the carboxylic acids on the one hand, and *p*-nitrobenzonitrile on the other, can be readily reduced.

It was also hoped to oxidise the nitrile to 5-nitro-2-cyanobenzoic acid, but it was found to be impossible to prevent the hydrolysis of the cyano-group. Oxidation with alkaline permanganate affords a most convenient method, however, for the preparation of 5-nitrophthalic acid, "β-nitrophthalic acid," m. p. 162°.

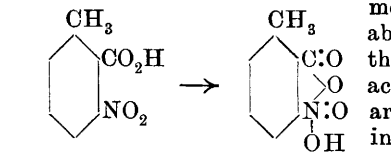
A solution of 3-nitro-*o*-toluidine in glacial acetic acid was mixed with a little hydrochloric acid, diazotised with powdered sodium nitrite, and the product was then poured into the copper sulphate and

potassium cyanide solution as above. The 3-*nitro*-o-*toluonitrile* was purified by sublimation, and obtained in silky, yellow needles, m. p. 89—91°. This was hydrolysed by concentrated potassium hydroxide or moderately strong sulphuric acid to the new 3-*nitro*-o-*toluic acid*, $NO_2 \cdot C_6H_3Me \cdot CO_2H$, which was obtained in colourless, silky needles, m. p. between 200° and 210°. The constitution was proved by converting the acid into *m*-nitrotoluene. The acid sublimes when slowly heated, and is fairly soluble in water but not in cold alcohol. The indefinite melting point distinguishes the acid from the nine nitrotoluic acids of proved constitution, and the solubility relationships do not accord with the descriptions of four nitrotoluic acids of unknown structure.

The *sodium*, *potassium*, *ammonium*, *silver*, *lead*, *copper*, *magnesium*, *barium*, *calcium*, *zinc*, and *aluminium* salts of 3-nitro-*o*-toluic acid are described, and a small amount of the *methyl* ester, m. p. 72—75°, was obtained by means of methyl sulphate. The acid illustrates the ester rule, for the two ortho-substituents almost prohibit esterification.

Either the nitrile or the 3-nitro-*o*-toluic acid yielded 1-nitrophthalic acid, "α-nitrophthalic acid," on oxidation with alkaline permanganate. An attempt was made to reduce the acid by means of tin and hydrochloric acid to 3-amino-*o*-toluic acid, but this could not be isolated, for, on evaporation, it changed into *m*-toluidine. It was indeed formed, however, for 3-hydroxy-*o*-toluic acid was obtained on diazotising the solution of the reduction product. The latter solution was also diazotised and heated with the potassium-cuprous cyanide solution, when 1-methyl-*o*-phthalic acid was obtained, and it was finally evaporated nearly to dryness in a vacuum, the residue was acetylated, then oxidised and subsequently hydrolysed, and thus converted into 1-aminophthalic acid.

The 3-nitro-*o*-toluic acid undergoes certain physical changes when exposed to the air for several days. It becomes less soluble in water, more so in organic media, and melts at about 180—185° (decomp.), thus acquiring the properties of the isomeric nitrotoluic acids. It is assumed that the differences are due to the tautomerism expressed as in the annexed formulæ.



Some interesting generalisations with regard to the melting points and colours of the nitrotoluidines and nitrotoluonitriles are developed. Of the ten nitrotoluidines and eight nitrotoluonitriles, the most fusible are those in which the nitro-group is ortho to the methyl group. J. C. W.

Supposed Instability of High-Molecular Imino-acids. N. A. Schlezinger (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1183—1190).—From the failure of his attempts to prepare propioimino*cyclo*heptanecarboxylic and iminodiphenylacetic acids, Stadnikov ("The Amino-, Imino-, and Nitrilo-acids," Moscow, 1910), assumes that these acids are unstable, and concludes that the stability of imino-acids and their derivatives diminishes as the molecular magnitude of the acid increases. The author shows, however, that this supposed effect of the entrance of heavy radicles in the molecule has no real existence, and that

s-iminodiphenylacetic acid is not only readily prepared but stable towards boiling acids in concentrated solution. The conditions employed by Stadnikov lead to decomposition of the nitrilo-ester in the sense of the equation,

$$CN\cdot CHPh\cdot NH\cdot CHPh\cdot CO_2Et + 2H_2O = EtOH + Ph\cdot CHO + HCN + NH_2\cdot CHPh\cdot CO_2H.$$

An exactly similar decomposition was observed by the author with the nitriles of ethylenebis-imino-acids (this vol., i, 506). The molecules of the nitriles of imino- (and also amino-, nitrilo-, and bis-imino-) acids contain two atomic groupings, namely, the imino- and the nitrile groups, capable of undergoing change on hydrolysis. It is very probable that, in the decomposition according to the equation, $NHR''\cdot CHRR'\cdot CN + H_2O = RR'\cdot CO + HCN + NH_2R''$ (I), the first product is the ammonium compound, $OH\cdot NH_2R''\cdot CHRR'\cdot CN$ (*A*). In acid solution, compound *A* occurs together with the salt,

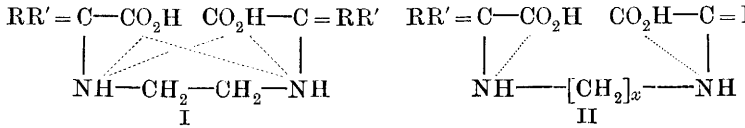
$$NH_2R''X\cdot CHRR'\cdot CN\ (B),$$

and increase of the concentration of the acid, HX, may lower the concentration of *A* and increase that of *B* to such an extent that decomposition according to scheme I becomes practically impossible. Hydrolysis of the nitrile would then proceed entirely according to the equation

$$NHR''\cdot CHRR'\cdot CN + 2H_2O = NH_3 + NHR''\cdot CHRR'\cdot CO_2H\ (II).$$

Experiment confirms these conclusions, since hydrolysis of the nitrilo-esters by concentrated sulphuric acid, instead of by fuming hydrochloric acid, leads to the formation of *s*-di-iminodi-phenylacetic acid. The final result in any particular case depends partly on the relative velocities of two competing reactions and partly on the effective relative concentrations of the hydroxide *A* and the salt *B*, these depending on the equilibrium constant of the reaction, $A + HX = B + H_2O$, that is, on the extent to which the basic properties of the imino-group of the nitrile are developed. The basicity of the imino-group is influenced by the number and distribution of the electronegative groups in the molecule, and it is the influence of the two phenyl groups in this direction and not their mass, which accounts for the so-called instability of the nitrilo-ester of iminodiphenylacetic acid. A similar explanation is applicable in the case of the bisimino-acids.

In view of the pronounced insolubility of ethylenebisimino-acids, the author regards them as of configuration I, whereas tri-, penta-, and hepta-methylenebisimino-acids have structures (II) perfectly analogous to those of ordinary amino-acids:



I II

Iminodiphenylacetic acid, $CO_2H\cdot CHPh\cdot NH\cdot CHPh\cdot CO_2H$, prepared from the nitrilo-ester, $CN\cdot CHPh\cdot NH\cdot CHPh\cdot CO_2Et$ (compare Stadnikov, *loc. cit*) by the action of sulphuric acid, forms spherical aggregates of slender needles, or opaque nodules, decomposing at about 199° in a sealed capillary. It is monobasic towards methyl orange, and dibasic

towards phenolphthalein. Its *hydrochloride*, *copper*, and *nickel* ($+3H_2O$) salts and *methyl* ester, which forms a viscous syrup, D_4^{20} 1·1550, n_D^{20} 1·5413, were prepared. T. H. P.

Action of Sunlight on the Cinnamic Acids. A. W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 181—184. Compare this vol., i, 535).—Further experiments on the action of sunlight on the cinnamic acids have shown that α-storax-cinnamic acid yields α-truxillic acid, whilst β-truxillic acid is formed from β-storax-cinnamic acid. The truxillic acids are supposed to be polymerisation products corresponding with the formulæ

$$\begin{matrix} C_6H_5\cdot CH\cdot CH\cdot CO_2H \\ CO_2H\cdot CH\cdot CH\cdot C_6H_5 \end{matrix} \qquad \begin{matrix} C_6H_5\cdot CH\cdot CH\cdot CO_2H \\ C_6H_5\cdot CH\cdot CH\cdot CO_2H \end{matrix}$$

α-acid. β-acid.

The formation of these different products from the α- and β-cinnamic acids may possibly be due to a difference in the disposition of the molecules in the crystals, or, if it is assumed that the molecules of the solid are double molecules, to a difference in the structure of the double molecules. H. M. D.

Bimolecular Nitriles. E. VON MEYER (*J. pr. Chem.*, 1915, **92**, 174—193. Compare A., 1914, i, 996).—Further studies of the so-called dinitriles, $NH{:}CR\cdot CH_2\cdot CN$ or $NH_2\cdot CR{:}CH\cdot CN$.

I. *Reactions between Dinitriles and Ketones.* [Preliminary note.] Dinitriles which can react in the amino-form condense with ketones to form derivatives of 1 : 4-dihydropyridine. Much work had been completed in this direction (with KURT WAGNER) but the details have been lost and the new compounds must be prepared afresh. The ketones show a similar gradation in activity towards the dinitriles to that which they exhibit towards phenylhydrazine (compare Petrenko-Kritschenko).

II. *New Dinitriles. Derivatives of Benzoacetodinitrile.* [With ELISABETH SPRECKELS]. Various nuclear-substitution products of benzonitrile have been condensed with acetonitrile in the presence of granulated sodium, and typical derivatives of the new dinitriles have been prepared.

A. o-Chlorobenzonitrile yielded o-*chlorobenzoacetodinitrile*,

$$C_6H_4Cl\cdot C(NH)\cdot CH_2\cdot CN,$$

white, somewhat cubical crystals, m. p. 106—107°, which was hydrolysed by alcoholic hydrochloric acid to o-*chlorophenyl cyanomethyl ketone*, $C_6H_4Cl\cdot CO\cdot CH_2\cdot CN$, cubes, m. p. 101° (*benzylidene* compound, $C_6H_4Cl\cdot CO\cdot C(CN){:}CHPh$, glistening flakes, m. p. 90°). The dinitrile was also condensed with phenylhydrazine acetate to 2-*imino*-1-*phenyl*-4-o-*chlorophenylpyrazolone*, $NPh\begin{matrix} N{=}\!\!-\!\!-C\cdot C_6H_4Cl \\ C(NH)\cdot CH_2 \end{matrix}$, needles, m. p. 137°, and with benzaldehyde to 3 : 5-*dicyano*-4-*phenyl*-2 : 6-*di*-o-*chlorophenyl*-1 : 4-*dihydropyridine*, $C_{25}H_{15}N_3Cl_2$, slender, white crystals, m. p. 260°.

B. The corresponding para-compounds :—p-*chlorobenzoacetodinitrile*, pale yellow needles, m. p. 144°; p-*chlorophenyl cyanomethyl ketone*, pale

yellow needles, m. p. 127° (*benzylidene* compound, m. p. 125°); *pyrazolone* derivative, needles, m. p. 185°; *dihydropyridine* derivative, slender needles, m. p. 233°.

C. The meta-series :—m-*chlorobenzoacetodinitrile*, long, stout prisms, m. p. 86°; m-*chlorophenyl cyanomethyl ketone*, small leaflets, m. p. 81° (*benzylidene* compound, felted needles, m. p. 118°); *pyrazolone* derivative, m. p. 108°; *dihydropyridine* derivative, m. p. 248°. The three chlorophenyl cyanomethyl ketones formed the phenylhydrazone of benzaldehyde when treated with phenylhydrazine.

D. *p*-Ethoxybenzonitrile (from *p*-phenetidine) gave a high yield of p-*ethoxybenzoacetodinitrile*, $OEt\cdot C_6H_4\cdot C(NH)\cdot CH_2\cdot CN$, glistening leaflets, m. p. 136·5°, which was hydrolysed to p-*ethoxyphenyl cyanomethyl ketone*, $OEt\cdot C_6H_4\cdot CO\cdot CH_2\cdot CN$, m. p. 123°, and condensed with phenylhydrazine to 2-*imino*-1-*phenyl*-4-p-*ethoxyphenylpyrazolone*, $C_{17}H_{17}ON_3$, prisms, m. p. 188°, with hydroxylamine to 2-*imino*-4-p-*ethoxyphenyl*iso-*oxazolone*, $OEt\cdot C_6H_4C\cdot\begin{matrix}N\text{—}O\\ |\\ CH_2\cdot C:NH\end{matrix}$, needles, m. p. 127°, with benzaldehyde to 3 : 5-*dicyano*-4-*phenyl*-2 : 6-*di*-p-*ethoxyphenyl*-1 : 4-*dihydropyridine*, $C_{29}H_{25}O_2N_3$, m. p. 194°, and with methyl ethyl ketone (see under I) to 3 : 5-*dicyano*-2 : 6-*di*-p-*ethoxyphenyl*-4-*methyl*-4-*ethyl*-1 : 4-*dihydropyridine*, $C_{26}H_{27}O_2N_3$, fibrous crystals, m. p. 116°.

E. *p*-Dimethylaminobenzonitrile (from *p*-dimethylaminobenzaldoxime) gave a moderate yield of p-*dimethylaminobenzoacetodinitrile*, $NMe_2\cdot C_6H_4\cdot C(NH)\cdot CH_2\cdot CN$, pale yellow leaflets, m. p. 210°, and this was hydrolysed to p-*dimethylaminophenyl cyanomethyl ketone*, $NMe_2\cdot C_6H_4\cdot CO\cdot CH_2\cdot CN$, glistening leaflets, m. p. 166°.

III. *Hydrazine Derivatives of Acetodinitrile.*—Three compounds, *A*, *B* and *C*, were originally obtained by the action of hydrazine on acetodinitrile (A., 1895, i, 583). Of these, *B* cannot now be prepared, and further reactions of *A* and *C* are described which throw some light on their structures. *A* can be diazotised in the presence of hydrochloric acid, whilst with nitrous fumes alone it forms an *oximino*-compound, $C_8H_9ON_5$, m. p. 167° (decomp.). It also yields an *acetyl* compound, silky needles, m. p. 140°, and a *phenylcarbamide*, $C_{15}H_{15}ON_5$, m. p. 188°. The isomeride, *C*, can also be diazotised, converted into an *acetyl* compound, $C_{10}H_{12}ON_4$, m. p. 106°, and a *phenylcarbamide*, $C_{15}H_{15}ON_5$, m. p. 137°, but it yields no nitroso-compound. It is assumed that the primary product of the action of hydrazine on acetodinitrile is the hydrazone, which then reacts with more acetodinitrile in its amino-form, thus; $NH:CMe\cdot CH_2\cdot CN + N_2H_4 \longrightarrow CN\cdot CH_2\cdot CMe:N\cdot NH_2$; this $+ NH_2\cdot CMe:CH\cdot CN \longrightarrow CN\cdot CH_2\cdot CMe:N\cdot NH\cdot CMe:CH\cdot CN + NH_3$. The product then undergoes rearrangement into the compound *A*, which can behave in the two tautomeric forms, $\begin{matrix}CMe\text{=}\!\!=\!\!=N\\ |\\ CH_2\cdot C(:NH)\end{matrix}\!\!>N\cdot CMe:CH\cdot CN$ and $\begin{matrix}CMe\text{=}\!\!=\!\!=N\\ |\\ CH:C(NH_2)\end{matrix}\!\!>N\cdot CMe:CH\cdot CN$, or be further rearranged, by boiling with concentrated hydrochloric acid, into the compound *C*, $\begin{matrix}CMe:N\cdot N\cdot CMe:CH\\ |\quad\quad\quad\quad\quad\quad|\\ CH\text{=}\!\!=\!\!=C\cdot N\text{=}\!\!=C\cdot NH_2\end{matrix}$.

IV. *Nitrogen-halogen Derivatives of Dinitriles.*—Chloro- and bromo-acetodinitriles have long been known (*ibid.*). *Iodoacetodinitrile*, $CN\cdot CH_2\cdot CMe{:}NI$, has now been obtained by adding a solution of iodine in potassium iodide to aqueous acetodinitrile, as a white precipitate, m. p. 85°. It can be titrated with thiosulphate in the presence of hydrochloric acid, and the other halogen derivatives can likewise be titrated if potassium iodide is also added.

V. N-*Aryl Derivatives of Dinitriles* (compare A., 1908, i, 909). Benzoacetodinitrile condenses with aniline acetate when heated in a sealed tube at 120—130°, to form N-*phenylbenzoacetodinitrile*, $CN\cdot CH_2\cdot CPh{:}NPh$, in pale yellow crystals, m. p. 187°. N-*Phenyl*-p-*toluacetodinitrile*, $CN\cdot CH_2\cdot C(NPh)\cdot C_6H_4Me$, m. p. 189°, is prepared in the same way. Acetodinitrile reacts more readily with bases, even in cold aqueous solutions; thus with *p*-phenylenedimethyldiamine it yields N-p-*dimethylaminophenylacetodinitrile*,

$$CN\cdot CH_2\cdot CMe{:}N\cdot C_6H_4\cdot NMe_2,$$

pale red leaflets, m. p. 151°, and with *p*-anisidine, N-p-*methoxyphenylacetodinitrile*, m. p. 123°. When treated with nitrous fumes in acetic acid solution, *N*-phenylacetodinitrile (*ibid.*) yields a pale-yellow *oximino*-compound, $NPh{:}CMe\cdot C(CN){:}N\cdot OH$, and a *compound*, insoluble in alkalis, which is regarded as a condensation product of the nitroso-compound with unchanged *N*-phenylacetodinitrile, thus, $NPh{:}CMe\cdot C(CN){:}N\cdot CH(CN)\cdot CMe{:}NPh$. The latter is a brick-red substance, m. p. 270°. The above *p*-methoxyphenylacetodinitrile only yields an *oximino*-compound, $OMe\cdot C_6H_4\cdot N{:}CMe\cdot C(CN){:}N\cdot OH$, m. p. 155°. J. C. W.

Preparation and Decomposition of Phenylnitroformaldehydephenylhydrazone. R. Ciusa and G. Benelli (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 20—25).—The decomposition by heat of phenylnitroformaldehydephenylhydrazone,

$$NO_2\cdot CPh{:}N\cdot NHPh = (\cdot CPh{:}N\cdot NHPh)' + NO_2$$

(compare Ciusa and Toschi, A., 1914, i, 334), is similar to that of nitrosobenzaldehydephenylhydrazone,

$$2NO\cdot CPh{:}N\cdot NHPh = (\cdot CPh{:}N\cdot NHPh)_2 + 2NO$$

(compare Bamberger and Pemsel, A., 1903, i, 285), and both these decompositions resemble those of triphenylnitromethane, triphenylnitrosomethane, and nitrosodiphenylamine, $CPh_3\cdot NO_2 \rightleftarrows CPh_3 + NO_2$; $CPh_3\cdot NO \rightleftarrows CPh_3 + NO$, and $NPh_2\cdot NO \rightleftarrows NPh_2 + NO$.

The best method of studying the decomposition of the nitrohydrazones consists in heating in a reflux apparatus a solution of the dry nitrohydrazone in xylene which has been dried over sodium, the elimination of the nitrogen peroxide being facilitated by means of a current of dry nitrogen. In this way, phenylnitroformaldehydephenylhydrazone yields (1) a proportion of nitrogen peroxide varying with the rapidity of heating and of the passage of nitrogen and with the amount of moisture present, and (2) the *compound*,

$$CHPh{:}N\cdot NPh\cdot C_6H_2Me_2\cdot NO_2,$$

which crystallises in white needles, m. p. 170°, gives phenylhydrazine when hydrolysed with sulphuric acid, and is formed as the result of the following series of changes: $NO_2\cdot CPh{:}N\cdot NHPh = NO_2 +$

(CPh:N·NHPh); the latter $+C_6H_4Me_2 = C_6H_3Me_2\cdot CPh{:}N\cdot NHPh +$ CHPh:N·NHPh and $C_6H_3Me_2\cdot CPh{:}N\cdot NHPh + NO_2 \longrightarrow$ $NO_2\cdot C_6H_2Me_2\cdot CPh{:}N\cdot NHPh$, and (3) a small proportion of a red compound, m. p. 195°, which may represent the product of the action of nitrogen peroxide on the benzaldehydephenylhydrazone formed as shown under (2).

The action of nitrogen peroxide on benzaldehydephenylhydrazone in ethereal solution (compare Ciusa and Pestalozza, A., 1908, i, 833) yields: (1) as principal product phenylnitroformaldehydephenylhydrazone; (2) benzenediazonium nitrate; (3) dibenzylidenediphenylhydrotetrazone; (4) an *isomeride* of (1), forming silky, red needles, m. p. 135°, and giving a green solution in concentrated sulphuric acid; this compound and compound (1) are probably stereoisomerides having the respective formulæ $\begin{matrix} Ph\cdot C\cdot NO_2 \\ \| \\ N\cdot NHPh \end{matrix}$ and $\begin{matrix} Ph\cdot C\cdot NO_2 \\ \| \\ Ph\cdot NH\cdot N \end{matrix}$; (5) a compound, $C_{28}H_{26}O_3N_6$, which forms dark red needles, m. p. 183°, and was obtained (but not analysed) by Bamberger and Pemsel (*Ber.*, 1903, **36**, 84; A., 1903, i, 283) among the secondary products of the oxidation of benzaldehydephenylhydrazone by amyl nitrite: (6) a small proportion of a compound, which forms yellowish needles, m. p. 202—204°, and is possibly tetraphenyltetrazoline (compare Bamberger and Pemsel, *loc. cit.*). T. H. P.

Gallaldehyde Trimethyl Ether and Syringaldehyde. F. Mauthner [With G. Szönyi] (*J. pr. Chem.*, 1915, [ii], **92**, 194—201; compare A., 1908, i, 348, 729; 1913, i, 277).—These aldehydes have been treated with magnesium alkyl iodides, and nitromethane, and also employed in the synthesis of chalkones by Kostanecki's method.

A benzene solution of gallaldehyde trimethyl ether was shaken with an ethereal solution of magnesium methyl iodide, whereby the normal product, namely, 3 : 4 : 5-*trimethoxyphenylmethylcarbinol*, $C_{11}H_{16}O_4$, was obtained, as a colourless oil, b. p. 179—180°/11 mm. This was oxidised by chromic acid mixture to 3 : 4 : 5-trimethoxyacetophenone (A., 1910, i, 680). The similar 3 : 4 : 5-*trimethoxyphenylethylcarbinol*, $C_{12}H_{18}O_4$, b. p. 184—185°/11 mm., was oxidised to 3 : 4 : 5-*trimethoxypropiophenone* (3 : 4 : 5-*trimethoxyphenyl ethyl ketone*), a pale yellow oil, which was characterised by a *nitrophenylhydrazone*, $C_{18}H_{21}O_5N_3$, reddish-brown needles, m. p. 170—171°.

Gallaldehyde trimethyl ether and gallacetophenone trimethyl ether (*ibid.*) were left in a warm alcoholic solution of sodium hydroxide when 3 : 4 : 5 : 3′ : 4′ : 5′-*hexamethoxychalkone* [3 : 4 : 5-*trimethoxyphenyl* 3 : 4 : 5-*trimethoxystyryl ketone*], $C_{21}H_{24}O_7$, separated in pale yellow leaflets, m. p. 128—129°. The same aldehyde was also condensed with acetoveratrone (3 : 4-dimethoxyacetophenone) yielding 3 : 4 : 5 : 4′ : 5′-*pentamethoxychalkone* [3 : 4-*dimethoxyphenyl* 3 : 4 : 5-*trimethoxystyryl ketone*], $C_{20}H_{22}O_6$, in pale yellow leaflets, m. p. 131—132°.

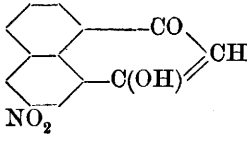
A mixture of gallaldehyde trimethyl ether and diazomethane in alcohol was carefully treated with alcoholic potassium hydroxide at −5°, then mixed with ice and water and finally acidified, when *ω-nitro*-3 : 4 : 5-*trimethoxystyrene*, $C_{11}H_{13}O_5N$, separated in yellow leaflets,

m. p. 119—120°. Syringaldehyde yielded under the same conditions, *ω-nitro-4-hydroxy-3 : 5-dimethoxystyrene*, $C_{10}H_{11}O_5N$, m. p. 115—116°.

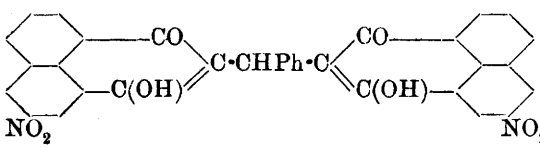
Syringaldehyde was also mixed with hippuric acid and anhydrous sodium acetate and then heated with acetic anhydride, when *α-benzoylimino-3 : 5-dimethoxy-4-acetoxycinnamic anhydride*, $C_{20}H_{17}O_6N$, was obtained in lemon-yellow needles, m. p. 212—213°. J. C. W.

Action of Grignard's Reagent on Hydroxy-ketonic Dyestuffs and their Ethers. ARABINDA SIRKER (T., 1915, **107**, 1241—1247).—Magnesium ethyl iodide reacts with alizarin dimethyl ether to give small yields of *10-hydroxy-5-keto-1 : 2-dimethoxy-10-ethyldihydroanthracene* and *5 : 10-dihydroxy-1 : 2-dimethoxy-5 : 10-diethyldihydroanthracene* respectively, according as to whether sufficient organo-magnesium compound is present to react with only one, or with both ketonic groups. The former substance forms reddish-yellow needles, m. p. 188°, and the latter crystallises in crimson needles, m. p. 149°. On demethylation by treatment with aluminium chloride, *1 : 2 : 10-trihydroxy-5-keto-10-ethyldihydroanthracene*, red needles, m. p. 275°, and *1 : 2 : 5 : 10-tetrahydroxy-5 : 10-diethyldihydroanthracene*, brown needles, m. p. 198°, were formed from their corresponding ethers. These compounds showed no tendency to lose water and assume a permanently quinonoid structure as did similar derivatives of quercetin (Watson and Sen, T., 1914, **105**, 389), and accordingly no remarkable difference in dyeing properties from those of alizarin was observed. The action of the Grignard reagent prepared from bromoanisole on 7-ethoxy-γ-benzopyrone was also investigated. The de-ethylated product was not inviting as a dye and was not further studied. With *ethyl 7-ethoxy-γ-benzopyrone-2-carboxylate*, colourless needles, m. p. 118°, the above Grignard reagent gave a tarry product, from which only unchanged ester could be isolated. G. F. M.

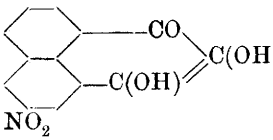
3-Nitrohydroxyketo*peri*naphthindene. E. CALDERARO (*Gazzetta*, 1915, **45**, ii, 131—138).—*3-Nitrohydroxyketo*perinaphthindene (annexed formula), prepared by the condensation of 3-nitronaphthalic anhydride with ethyl malonate in presence of fused zinc chloride, forms minute, orange-yellow needles, and blackens without melting at 300°. With concentrated sulphuric acid it gives a red solution, and it dissolves readily in cold alkali carbonate or hydroxide solution with formation of an intense red coloration. The following derivatives were prepared: *sodium*, $C_{13}H_6O_4NNa$: *methyl ether*, $C_{14}H_9O_4N$, which crystallises in yellow, spherical masses, softening at 230°, m. p. 245°; *ethyl ether*, which forms a deep reddish-brown, hard, crystalline crust, m. p. 195—197°; and *acetate*, $C_{15}H_9O_5N$, which forms hard, yellowish-brown globules, m. p. 194—195°.



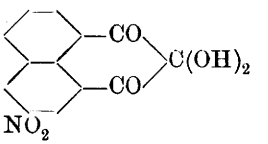
With benzaldehyde in presence of pyridine it condenses to the *compound* (annexed formula), which forms minute, bright red crystals, m. p. 275—276°(decomp.), and dissolves readily in alcoholic alkali solution, giving an intensely red liquid.



3-*Nitrodihydroxyketo*peri*naphthindene* (annexed formula), obtained by the action of phenylhydrazine in acetic acid solution on 3-nitrohydroxyketo*peri*-naphthindene or by reduction of the triketone (*vide supra*) by means of hydrogen sulphide, forms bright red, flocculent crystals, m. p. 265—266° (decomp.), reduces ammoniacal silver nitrate solution, dissolves in hot bromine water giving the triketone, and in dilute aqueous alkali hydroxides forms reddish-violet solutions, becoming blue on further addition of the hydroxide.



The *hydrate* of 3-*nitro*peri*naphthindantrione* (annexed formula), obtained by treating with bromine water the crude product of the action of phenylhydrazine on the nitrohydroxyketone, forms orange-yellow needles, and at temperatures above 100° is converted into the reddish-brown 3-*nitro*peri*naphthindantrione*, $NO_2 \cdot C_{10}H_5 \langle \begin{matrix} CO \\ CO \end{matrix} \rangle CO$, m. p. 172—173° (decomp.), which reduces ammoniacal silver nitrate and, in aqueous solution, dyes paper blue; the *phenazine* of the triketone, $NO_2 \cdot C_{10}H_5 \langle \begin{matrix} C{:}N \\ CO \cdot C{:}N \end{matrix} \rangle C_6H_4$, forms minute, yellow needles, m. p. 276—277°. T. H. P.



Action of Ozone on Organic Compounds. IV. C. HARRIES (*Annalen*, 1915, **410**, 1—116. Compare A., 1906, i, 225; 1910, i, 607; 1912, i, 673).—The author calls attention to the advantages of the ozone method over that of catalytic reduction for investigating the constitution of organic compounds. A difficulty in the former method, which has not yet been entirely overcome, is the formation, during the decomposition of ozonides by water or glacial acetic acid, of very stable peroxides, the presence of which hinders the isolation of aldehydes and ketones by means of the usual reagents.

[With RICHARD SEITZ.] Using unwashed ozone, Neresheimer (A., 1908, i, 194) obtained from pinene a solid and a liquid ozonide, neither of which had the normal composition. It has now been found that the action of 4·8—9·3% washed ozone (with 5% sodium hydroxide and concentrated sulphuric acid) on pinene (b. p. 46°/11 mm., from French turpentine) in hexane results in the formation of a colourless, solid *ozonide*, $C_{10}H_{16}O_3$, which is insoluble in ether; in addition to this, a syrupy and an oily fraction have been obtained, which contain an ozonide.

When *cyclo*hexene in hexane is treated with washed 6—9% ozone, a solid ozonide is precipitated and a liquid *ozonide*, $C_6H_{10}O_3$, remains in the mother liquor. The latter has b. p. 47—52°/10 mm., is a mobile, highly refractive liquid having a powerful, unpleasant odour, and is only slightly explosive. The solid *ozonide*, which is probably dimeric, $(C_6H_{10}O_3)_2$, is also formed when the strongest, unwashed ozone is used. It has m. p. 60—65°, explodes violently at about 140—150°, and is decomposed by water at 120—125°, yielding *cyclo*pentenaldehyde,

adipodialdehyde, the aldehydo-acid, and adipic acid. The *α*- and *β-cyclo*hexenozonides described by Splawa-Neyman (A., 1908, i., 967) are to be regarded as polymeric *cyclo*hexenozonide and polymeric *cyclo*hexenoxozonide repectively.

[With HANS WAGNER.] *cyclo*Pentene yields different products according to the conditions under which it is ozonised. Dissolved in hexane and treated with washed ozone in a freezing mixture, it yields a liquid, monomeric ozonide identical with that described by Tank (A., 1908, i, 517). Treated slowly with washed 5% ozone in ethyl chloride cooled by carbon dioxide and ether, it yields a colourless, crystalline *ozonide* (probably dimeric), $(C_5H_8O_3)_2$, which explodes violently at 94°, and is decomposed by water much more rapidly than the dimeric *cyclo*hexenozonide.

By exposure to strong sunlight the liquid ozonide is converted into a polymeric, non-explosive, microcrystalline ozonide. Treated with the strongest, unwashed ozone, *cyclo*pentene yields the normal liquid ozonide when dissolved in carbon tetrachloride, but in chloroform solution a liquid, monomeric *oxozonide*, $C_5H_8O_4$, and a white, crystalline, dimeric *oxozonide*, which is very explosive and is very easily decomposed by water; the liquid oxozonide is yellow, has a very penetrating odour, is explosive, readily loses oxygen, forming the normal ozonide, and by keeping changes to a vitreous mass.

When *cyclo*pentanone is reduced by sodium and water in the presence of absolute ether, the only products are *cyclo*pentanol and the normal pinacone. When ordinary ether (containing ethyl alcohol) is employed, sodium ethoxide is formed, which exerts a condensing action, and the products of reduction contain, in addition to the preceding, 2-cyclo*pentyl*cyclo*pentanol*, $C_5H_9 \cdot C_5H_8 \cdot OH$, b. p. 116—117°/12 mm., which is oxidised to 2-*cyclo*pentyl*cyclo*pentanone by chromic and sulphuric acids at 30°; the latter forms a *benzylidene* derivative, $C_{17}H_{20}O$, faintly yellow needles, m. p. 97—98°, from which an oxime or a phenylhydrazone could not be obtained.

By heating with potassium hydrogen sulphate at 180—190°, 2-*cyclo*pentyl*cyclo*pentanol yields cyclo*pentyl*cyclo*pentene*, $C_{10}H_{16}$, b. p. 79/13° mm., $D_4^{22\cdot5}$ 0·8953, $n_D^{22\cdot5}$ 1·48627, n_α 1·48284, n_γ 1·49979, which is converted by washed ozone in light petroleum at 0° into a golden-yellow, viscous liquid; this is unstable, and appears to be a mixture of the normal ozonide and oxozonide

[With FRIEDRICH COMBERG.] Another attempt has been made to ascertain whether ozonisation causes a change in the position of a double linking. In 1896, Tiemann and Schmidt showed that the oxidation of citronellaldehyde by aqueous potassium permanganate only yielded products which were derivatives of a substance containing the group $CMe_2{:}CH\cdot$, not $CH_2{:}CMe\cdot CH_2\cdot$, present in citronellaldehyde. The ozonisation of the aldehyde (Harries and Himmelmann, A., 1908, i, 662) gave results indicating the presence of 40% of rhodinal, $CMe_2{:}CH\cdot[CH_2]_2\cdot CHMe\cdot CH_2\cdot CHO$. Since these results are not conclusive, Wagner has treated citronellaldimethylacetal in hexane with washed ozone at a low temperature, but again the results are indefinite; he discovered, in addition to the products of decomposition of the ozonide recorded by Harries and Himmelmann, a

new *keto-aldehyde*, $CH_3 \cdot CO \cdot [CH_2]_3 \cdot CHMe \cdot CH_2 \cdot CHO$. The authors have repeated the work, employing the latest methods of minimising the resinifying effect of acids and peroxides on the resulting aldehydes and ketones. The results, although not conclusive, are decidedly better than those obtained by the preceding investigators, and have demonstrated an entirely new reaction in the decomposition of ozonides. The ozonide is decomposed by boiling water and the resulting mixture is treated with ether. The ethereal solution is treated with calcium carbonate and water, and is thus separated into (1) the calcium salts of formic and β-methyladipic acids and the half-aldehyde of the latter, and (2) aldehydes, ketones, and peroxides, principally the last, from which acetone peroxide and *γ-methyloctan-η-one-α-al peroxide*, $CH_3 \cdot CO_2 \cdot [CH_2]_3 \cdot CHMe \cdot CH_2 \cdot CHO$, b. p. about 100°/14 mm., have been isolated. By treatment with 10% potassium carbonate at 50—60° or by boiling with 10% sodium hydroxide, the peroxides are decomposed and the following products have been isolated (1) an *aldehyde*, which forms a *semicarbazone*, $C_8H_{13}ON_3$, crystals, m. p. 181°, and is probably a *methylcyclopentenaldehyde*, (2) an *acid*, which forms a *silver* salt, $C_7H_9O_2Ag$, and is probably 5-*methylcyclopentene*-1-*carboxylic acid*, (3) 1-acetyl-4-methyl*cyclo*hexane, and (4) β-methyladipic acid and its half-aldehyde.

From the nature and quantity of the preceding decomposition products, the conclusion is drawn that commercial citronellaldehyde is a mixture of real citronellaldehyde and rhodinal in the ratio 40 : 60.

In 1898, Tiemann and Schmidt could obtain only one semicarbazone from commercial citronellaldehyde. This has been confirmed by the authors, and all attempts to separate the semicarbazone into two constituents by crystallisation have failed. By treatment, however, with washed ozone in ethyl acetate or carbon tetrachloride, the semicarbazone yields a *substance*, $C_{11}H_{21}O_5N_3$, decomp. about 55—60°, which appears to be an *oxozonide* and yields, by decomposition with boiling water, oxygen, carbon dioxide, formic acid, acetone peroxide, and two semicarbazones. One of these is the *semicarbazone*, yellowish needles, m. p. 185°, of methyloctanonal (derived from citronellaldehyde), whilst the other is the *semicarbazone*, m. p. 120—125°, of the half-aldehyde of β-methyladipic acid (derived from rhodinal). Hence the semicarbazone of commercial citronellaldehyde is either a very difficultly separable mixture of two semicarbazones or an individual substance in which a shifting of the double linking is produced by ozonisation.

The new type of decomposition of ozonides by water was discovered by the isolation of acetylcarbinol from the products of decomposition of citronellaldehyde ozonide. The keto-alcohol is probably formed owing to a change represented by the scheme:

$$O\langle\begin{matrix}CH_2\\O-O\end{matrix}\rangle CMe \cdot CH_2 \cdot \longrightarrow OH \cdot CH_2 \cdot COMe + \cdot CHO.$$

[With FRIEDRICH DÜVEL.] The so-called dimethylpiperidine, $C_7H_{15}N$, obtained together with piperylene by Hofmann in 1881 by the exhaustive methylation of piperidine, is shown to have the

constitution, $CH_2{:}CH{\cdot}[CH_2]_3{\cdot}NMe_2$, both by its synthesis and by its oxidation by ozone. Pentamethylene dibromide is heated at 80° with 33% absolute alcoholic trimethylamine and the resulting bis-quaternary ammonium bromide, $NMe_3Br{\cdot}[CH_2]_5{\cdot}NMe_3Br$, colourless crystals, m. p. above 300°, which loses hydrogen bromide and trimethylamine by crystallisation from alcohol, with the formation of the unsaturated quaternary *salt*, $CH_2{:}CH{\cdot}[CH_2]_3{\cdot}NMe_3Br$, stout prisms, is converted by treatment with water and silver oxide and subsequent distillation into trimethylamine and ε-dimethylamino-Δ^{α}-pentene (Hofmann's dimethylpiperidine), b. p. 118°, $D_4^{17\cdot5}$ 0·7548, $n_D^{17\cdot5}$ 1·42017, n_{α} 1·41706, n_{γ} 1·43174. This forms a *hydrogen oxalate*, $C_9H_{17}O_4N$, colourless crystals, m. p. 122°, and yields piperylene by exhaustive methylation. By ozonisation in dilute hydrochloric acid and decomposition of the ozonide, it yields formaldehyde, the *hydrochloride*, needles, m. p. 146°, of γ-dimethylaminobutyric acid (the *platinichloride*, yellowish-brown crystals, has m. p. 170° [decomp.]), and *γ-dimethylaminobutaldehyde*, which cannot be isolated in a pure state since it readily changes, with loss of water, into a *substance*, $C_{12}H_{24}ON_2$, b. p. 142°/11 mm. γ-Dimethylaminobutaldehyde was characterised in the form of its *diethylacetal*, $C_{10}H_{23}O_2N$, b. p. 94—95°/11 mm., $D_4^{20\cdot5}$ 0·8662, $n_D^{20\cdot5}$ 1·42267, which yields a *hydrogen oxalate*, leaflets, m. p. 118°, *picrate*, yellow prisms, m. p. 113—114°, and *methiodide*, $C_{11}H_{26}O_2NI$, colourless powder, m. p. 50°, softening at 40°. The last derivative, by treatment with silver oxide and water, and subsequent distillation under diminished pressure, yields trimethylamine and crotonaldehydediethylacetal, a change in the position of the double linking also occurring. A change in the position of the double linking of ε-dimethylamino-Δ^{α}-pentene does not readily occur, since the substance can be recovered unchanged after being boiled with amyl alcohol and sodium amyloxide.

[With George Francis Morrell.] Partly an account of work already published (A., 1911, i, 914). 2-Benzoylamino-4-acetyl-1-methyl*cyclo*hexane cannot be hydrolysed without decomposition; it forms a p-*nitrophenylhydrazone*, yellow needles, m. p. 252°, and a *semicarbazone*, colourless, microscopic needles, m. p. about 200°. The corresponding derivatives of *cis*-2-benzoylamino-1-methyl*cyclo*hexan-4-one have m. p. 248° (decomp.) and 194° (decomp.) respectively. By treatment with ozone in the same manner as the α-isomeride (*loc. cit.*) β-benzoyldihydroterpenylamine yields trans-2-*benzoylamino*-1-*methyl*-cyclo*hexan*-4-*one*, $C_{14}H_{17}O_2N$, needles, m. p. 150—151°.

The menthadiene, b. p. 63—65°/14 mm., obtained by the dry distillation of dihydroterpenylamine phosphate, appears to be identical with that obtained from dihydrocarvylamine (Harries, A., 1903, i, 743).

A method of reducing carvoxime with zinc dust in a mixture of alcohol and glacial acetic acid at 0° is described, whereby α-carvylamine containing only a small quantity of the β-isomeride is obtained in a yield of about 80%. It has b. p. 94—95°/12·5 mm., D_{19}^{19} 0·9168 $[\alpha]_D^{19}$ +105·8°, n_D^{19} 1·49820, n_{α} 1·49474, and n_{γ} 1·51369; the hydrochloride has m. p. 220°, and the benzoyl derivative 174°, whereas

Goldschmidt gave 180° and 169° respectively for the two derivatives. Carvylamine forms, although with difficulty, a *dihydrochloride*, $C_{10}H_{18}NCl,HCl$, crystals, m. p. 145°, which yields a chlorinated base by treatment with alkalis, and is converted into terpenylamine and other substances by heating with pyridine at 100°.

[With SYDNEY SMITH.] This work is a continuation of that of Morrell, its object being the preparation of 2-amino-4-acetyl-1-methyl-*cyclo*hexane by the hydrolysis of its acyl derivatives. For this purpose the carbethoxy-derivative is suited best, the acetyl, formyl, and oxalyl derivatives being less so. By oxidation with unwashed 10—12% ozone in glacial acetic acid acetyldihydrocarvylamine yields *2-acetylamino-4-acetyl-1-methylcyclohexane*, slender needles, m. p. 193—194°, which is unchanged by concentrated hydrochloric acid at 120° and forms a *semicarbazone*, crystals, m. p. 234—235° (decomp.), *p-nitrophenylhydrazone*, m. p. 229° (decomp.), and *oxime*, decomp. 221°. Dihydrocarvylamine and boiling, anhydrous formic acid yield a *substance*, $C_{11}H_{19}ON$, slender needles, m. p. 152—153°, which is probably formyldihydroterpenylamine. By heating with ethyl formate at 125°, dihydrocarvylamine yields the *formyl* derivative, b. p. 179—180°/15 mm., which is oxidised by ozone to *2-formylamino-4-acetyl-1-methylcyclohexane*, colourless prisms, m. p. 120—121° (*oxime*, $C_{10}H_{18}O_2N_2$, slender needles, m. p. about 179°; *p-nitrophenylhydrazone*, yellow needles, decomp. 239°; *semicarbazone*, m. p. 201° [decomp.]).

Dihydrocarvylamine and ethyl oxalate at 135° yield the *oxalyl* derivative, $C_2O_2(NH\cdot C_{10}H_{17})_2$, colourless needles, m. p. 250°, and the *semi-oxalyl* derivative, $C_{10}H_{17}\cdot NH\cdot CO\cdot CO_2Et$, colourless needles, m. p. 94°. The latter is oxidised by ozone to the *semi-oxalyl* derivative of 2-amino-4-acetyl-1-methyl*cyclo*hexane, $C_6H_9MeAc\cdot NH\cdot CO\cdot CO_2Et$, colourless needles, m. p. 107°, which forms an *oxime*, slender needles, m. p. 140° (decomp.), *p-nitrophenylhydrazone*, yellow needles, m. p. about 218—219° (decomp.), and *semicarbazone*, m. p. 168°.

By treating its boiling ethereal solution with potassium carbonate and ethyl chloroformate, dihydrocarvylamine is converted into its *carbethoxy*-derivative, colourless needles, m. p. 88°. This is oxidised by ozone to *2-carbethoxyamino-4-acetyl-1-methylcyclohexane*, colourless needles, m. p. 127°, which forms a *p-nitrophenylhydrazone*, yellow needles, m. p. 200°, *semicarbazone*, m. p. 181°, and *oxime*, slender needles, m. p. 144—145°, and is hydrolysed by concentrated hydrochloric acid at 105°, yielding the *hydrochloride*, $C_9H_{17}ON,HCl$, colourless needles, m. p. 183—185° (decomp.), of *2-amino-4-acetyl-1-methylcyclohexane*, m. p. 119—122°, b. p. 65—68°/11 mm. This forms an *oxime*, colourless needles, m. p. 151°, and a benzoyl derivative identical with that obtained by the oxidation of benzoyldihydrocarvylamine.

[With GEORG H. LÉNÁRT.] In the preparation of pyridine-2-aldehyde by the action of ozone on 2-styrylpyridine (A., 1914, i, 574) the other three possible products of decomposition of the ozonide, namely, benzoic acid, benzaldehyde, and α-picolinic acid, are also formed; a by-product is a *substance*, $C_{13}H_{12}NCl,HCl$, m. p. 153—154°, prisms.

Pyridine-2-aldehyde has D_4^{18} 1·1255, $n_D^{18\cdot5}$ 1·53886, n_α 1·53284, n_β 1·55396, n_γ 1·56749, forms a *hydrochloride*, C_6H_5ON,HCl,H_2O,

colourless prisms, m. p. 103—107°, and *picrate*, yellow needles, m. p. 101—102°, and reacts with concentrated, aqueous sodium hydrogen sulphite to form, not an additive compound, but a salt, probably the *hydrogen sulphite*, colourless needles, subliming at about 160°. The aldehyde forms a *p-nitrophenylhydrazone*, yellow powder, m. p. 235° (*hydrochloride*, reddish-yellow needles, m. p. 277° [decomp.]), *azine*, yellow needles or prisms, m. p. 149°, *anil*, b. p. about 165°/13 mm., and methiodide (phenylhydrazone, m. p. 244°; Kaufmann and Valette give 239—240°), and reacts with aqueous ammonia to form a *substance*, $(C_5NH_4\cdot CH{:}NH)_3$, faintly yellow needles, m. p. 126° (decomp.). The *diethylacetal*, $C_5NH_4\cdot CH(OEt)_2$, b. p. 110—112°/14 mm., is reduced by sodium and boiling ethyl alcohol to *piperidine-2-aldehyde diethylacetal*, b. p. 95—105°/14 mm., which forms the *hydrochloride* of *piperidine-2-aldehyde-p-nitrophenylhydrazone*, $C_{12}H_{16}O_2N_4,HCl$, yellow powder, m. p. 228° (decomp.), by treatment with hot hydrochloric acid and *p*-nitrophenylhydrazine.

Pyridine-2-aldehyde is converted by cold 50% potassium hydroxide into α-picolinic acid and *pyridine-2-carbinol*, $C_5NH_4\cdot CH_2\cdot OH$, b. p. about 112—113°/16—17 mm., which forms a *picrate*, golden-yellow crystals, m. p. 159°, and *platinichloride*, reddish-yellow needles, m. p. 179° (decomp.).

Pyridine-2-aldehyde is converted by aqueous potassium cyanide into *α-pyridoin* (*pyridylpicolinoylcarbinol*), $C_5NH_4\cdot CH(OH)\cdot CO\cdot C_5NH_4$, yellow needles, m. p. 156°, which is oxidised by concentrated nitric acid to *α-pyridil* (*di-2-pyridyl diketone*), $C_2O_2(C_5NH_4)_2$, pale citron yellow, rhombic crystals, m. p. 154—155° (*nitrate*, colourless, crystalline powder). Pyridine-2-aldehyde and α-picoline react in the presence of zinc chloride at 200° to form *s-di-2-pyridylethylene*, $C_2H_2(C_5NH_4)_2$, colourless needles, m. p. 118—119°, b. p. about 200°/17 mm., which forms a *dibromide*, $C_{12}H_{10}N_2Br_2$, colourless prisms, m. p. 153—154°.

Pyridine-2-aldehyde condenses with dimethylaniline in the presence of zinc chloride on the water-bath to form the *leuco-base*,

$$C_5NH_4\cdot CH(C_6H_4\cdot NMe_2)_2,$$

colourless leaflets or brownish crystals, m. p. 110°, which is oxidised by lead peroxide to a green dye comparable with malachite green.

In the presence of aqueous sodium hydroxide, pyridine-2-aldehyde condenses with *cyclo*-hexanone to form two *substances*, one of which, $C_{18}H_{16}ON_2$, colourless needles, m. p. 193°, probably has the formula $CO<\begin{matrix}C(:CH\cdot C_5NH_4)\cdot CH_2\\ C(:CH\cdot C_5NH_4)\cdot CH_2\end{matrix}>CH_2$, and the other, $C_{18}H_{20}O_3N_2$, yellow needles, m. p. 127°, the constitution,

$$CO<\begin{matrix}CH(CH[OH]\cdot C_5NH_4)\cdot CH_2\\ CH(CH[OH]\cdot C_5NH_4)\cdot CH_2\end{matrix}>CH_2.$$

Pyridine-3-aldehyde, b. p. 95—97°/15 mm., prepared from benzoylmetanicotine and ozone in a similar manner to pyridine-2-aldehyde (*loc. cit.*), shows in general the greatest similarity to this; the *phenylhydrazone*, m. p. 158°, forms pale yellow leaflets. C. S.

Synthesis of Indanediones. IV. Martin Freund and Karl Fleischer (*Annalen*, 1915, **409**, 268—290. Compare A., 1910, i, 490; 1913, i, 1073; 1914, i, 48).—In the earlier work indanediones

have been obtained by condensing aromatic hydrocarbons with substituted malonyl chlorides in the presence of aluminium chloride. It is now found that phenolic ethers behave in a similar manner. Thus quinol dimethyl ether and diethylmalonyl chloride in warm carbon disulphide yield, in the presence of aluminium chloride (1) an oil; (2) 4 : 7-*dimethoxy*-2 : 2-*diethylindane*-1 : 3-*dione*, $C_6H_2(OMe)_2\langle\begin{matrix}CO\\CO\end{matrix}\rangle CEt_2$, yellow prisms, m. p. 159—161°; and (3) 4-*hydroxy*-7-*methoxy*-2 : 2-*diethylindane*-1 : 3-*dione*, yellow needles, m. p. 105—106°, which is soluble in alkalis and forms an *acetate*, rosettes of colourless rhombohedra, m. p. 96—98°. Substances (2) and (3), by boiling with hydriodic acid, D 1·7, yield 4 : 7-*dihydroxy*-2 : 2-*diethylindane*-1 : 3-*dione*, pale yellow crystals, m. p. 90—94°. This compound and also (3) form intensely yellowish-green, fluorescent solutions in dilute alkalis, the fluorescence vanishing when the indandione ring is broken. For example, 4-hydroxy-7-methoxy-2 : 2-diethylindanedione is converted by boiling concentrated potassium hydroxide and subsequent acidification into 2-*hydroxy*-5-*methoxy*-ωω-*diethylacetophenone*-6-*carboxylic acid*,

$$CHEt_2\cdot CO\cdot C_6H_2(OH)(OMe)\cdot CO_2H,$$

colourless needles, changing at 75°, melting at 85°, and transparent above 90°, an alkaline solution of which is not fluorescent; a by-product of the reaction is a *substance*, $C_{14}H_{18}O_5,H_2O$, grey, crystalline powder, m. p. 103—105°, which appears to be a hydrate of the acid.

The oil (1), which is the chief product of the reaction, has b. p. 200°/15mm., D 1·314, contains one methoxyl group and is insoluble in alkalis. It has the composition $C_{14}H_{16}O_4$, and appears to be 4-*keto*-6-*methoxy*-3 : 3-*diethyl*-3 : 4-*dihydrocoumarin*, $OMe\cdot C_6H_3\langle\begin{matrix}CO\cdot CEt_2\\O—CO\end{matrix}\rangle$. It is converted by boiling hydriodic acid, D 1·7, into 6-*hydroxy*-4-*keto*-3 : 3-*diethyl*-3 : 4-*dihydrocoumarin*, almost colourless, crystalline powder, m. p. 128—130°, and by boiling concentrated potassium hydroxide into a *potassium* salt (which regenerates the original oil by solution in water) and a very small quantity of an *acid*, $C_{14}H_{18}O_5$, colourless crystals, m. p. 150—150·5°, which is probably α-2-*hydroxy*-5-*methoxybenzoyl*-α-*ethylbutyric acid*, $OMe\cdot C_6H_3(OH)\cdot CO\cdot CEt_2\cdot CO_2H$.

The condensation of veratrole and diethylmalonyl chloride in carbon disulphide in the presence of aluminium chloride leads to the formation of (1) 4 : 5-*dihydroxy*-2 : 2-*diethylindane*-1 : 3-*dione*, yellowish needles, m. p. 116—118°; (2) 5 : 6-*dihydroxy*-2 : 2-*diethylindane*-1 : 3-*dione*, colourless crystals, m. p. 216—218°, which exhibits a brownish-yellow fluorescence in alkaline solution and forms an *acetyl* derivative; m. p. 93—95°; (3) 5 : 6-*dimethoxy*-2 : 2-*diethylindane*-1 : 3-*dione*, colourless, rectangular plates, m. p. 149—151°, which forms a *nitro*-derivative, colourless, rhombic plates, m. p. 104—106°; and (4) 5-*hydroxy*-6-*methoxy*-2 : 2-*diethylindane*-1 : 3-*dione*, colourless needles, m. p. 106—108°, b. p. 210—230°/12 mm., which forms a yellow, crystalline *sodium* salt and yields a faint yellowish-green fluorescence in alkaline solution. By boiling with hydriodic acid (D 1·7), compounds (3) and (4) are converted into (2).

5 : 6-Dihydroxy-2 : 2-diethylindanedione is converted by boiling concentrated potassium hydroxide into 4 : 5-*dihydroxy*-ωω-*diethylaceto*-

phenone-2-carboxylic acid, $CHEt_2\cdot CO\cdot C_6H_2(OH)_2\cdot CO_2H$, faintly yellow, microscopic crystals, m. p. 177° (decomp.), which forms an intensely yellowish-green, non-fluorescent solution in dilute sodium hydroxide, and is converted above its m. p. into the *lactone*, $C_6H_2(OH)_2\langle{}^{CO\cdot O}_{---C:CEt_2}$, colourless, six-sided plates, m. p. 269—271°.

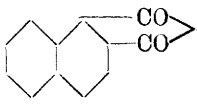
5-Hydroxy-6-methoxy-2 : 2-diethylindanedione forms an *acetyl* derivative, colourless prisms, m. p. 127—129°, and is converted by boiling concentrated potassium hydroxide into 4 (or 5)-*hydroxy*-5 (or 4)-*methoxy*-ωω-*diethylacetophenone*-2-*carboxylic acid*, colourless crystals, m. p. 149—151°, which forms a *diazine*,

$$OMe\cdot C_6H_2(OH)\langle{}^{CO\text{-------}NPh}_{C(CHEt_2):N},$$

colourless plates, m. p. 180—182°, by heating with phenylhydrazine, and is converted by boiling hydriodic acid (D 1·7), into the *lactone*, $C_6H_2(OH_2)\langle{}^{CO\cdot O}_{---CH\cdot CHEt_2}$, silvery grey leaflets, m. p. 202—203°, by the simultaneous elimination of a methyl group, loss of water, and reduction. C. S.

1 : 2-Naphthindanedione. F. Noto (*Gazzetta*, 1915, **45**, ii, 126—130).—In presence of sodium, ethyl phthalate condenses with ethyl acetate, giving diketohydrindene, whereas under similar conditions ethyl *peri*naphthalate does not react (compare Errera, A., 1911, i, 465). That this difference in behaviour is due, not to the presence of the benzene nucleus in the one case and of the naphthalene nucleus in the other, but to the different positions of the carboxyl groups in the two compounds, is shown by the fact that methyl naphthalene-1 : 2-dicarboxylate condenses with ethyl acetate and sodium, giving 1 : 2-naphthindanedione, which closely resembles diketohydrindene in its properties.

Methyl naphthalene-1 : 2-*dicarboxylate*, $C_{14}H_{12}O_4$, forms transparent, colourless crystals, m. p. 80°.



1 : 2-*Naphthindanedione* (annexed formula), forms long, slender needles, m. p. 180°, and dissolves in alkali solutions, giving a red coloration. When heated with alcoholic sodium hydroxide, it gives a sparingly soluble green compound, and when boiled with dilute hydrochloric acid a greenish-yellow compound, m. p. about 300°, which probably results from the condensation of 2 mols. of 1 : 2-naphthindanedione with elimination of $1H_2O$. The *sodium* salt of 1 : 2-naphthindanedione, $C_{13}H_7O_2Na$, crystallises with 1Et·OH. The bis*phenylhydrazone* of the diketone, $C_{10}H_6\langle{}^{C(:N_2HPh)}_{C(:N_2HPh)}\rangle CH_2$, forms shining, orange-yellow needles, m. p. 220° (decomp.). With benzaldehyde in alcoholic solution containing a drop of pyridine, 1 : 2-naphthindanedione condenses, giving the *compound* $C_{10}H_6\langle{}^{CO}_{CO}\rangle C:CHPh$, which crystallises in small, lemon-yellow needles, m. p. 190°.

When shaken with methyl sulphate in dilute potassium hydroxide solution, the naphthindanedione gives a *compound* which forms hard, reddish-yellow crystals, m. p. 118°, but was not obtained in sufficient quantity for investigation. Under similar conditions, the action of methyl sulphate on diketohydrindene yields a yellow compound, m. p. 206°, which dissolves in concentrated alkali hydroxide solution, giving a red and then a violet coloration, and is a product of the condensation of 2 mols. of diketohydrindene with elimination of $1H_2O$. A diethyl derivative of 1 : 2-naphthindanedione was obtained by Freund and Fleischer (A., 1910, i, 490) by the condensation of naphthalene with diethylmalonyl chloride in presence of aluminium chloride.

T. H. P.

Action of Light on Dibenzoylstyrene. E. Oliveri-Mandalà (*Gazzetta*, 1915, **45**, ii, 138—142. Compare Oliveri-Mandalà and Calderaro, A., 1914, i, 1077).—Further investigations have been made on the compound $C_{22}H_{16}O_2$, m. p. 118°, obtained by the action of light on dibenzoylstyrene in benzene solution. It is found that this compound forms long, yellow needles, m. p. 123—124°, and that it is not identical with the lactone of triphenylcrotonic acid. It yields the *monohydrazone*, $C_{22}H_{18}ON_2$, which forms a white, microcrystalline powder, m. p. 165°, and the mono-oxime, m. p. 175° (*loc. cit.*), and, when treated in absolute alcoholic solution with a current of hydrogen chloride, is converted into the trichlorofuran obtained under similar conditions from dibenzoylstyrene by Japp and Tingle (T., 1897, **71**, 1138).

As was shown by Japp and Wood (T., 1905, **87**, 709), the action of hydrazine on dibenzoylstyrene yields 3 : 4 : 6-triphenyl-1 : 2-diazine, whereas the isomeride, m. p. 123—124°, gives only a monohydrazone. On the assumption that the facility of reaction depends on the structure, the author ascribes (1) the *cis*-configuration to the dibenzoylstyrene (α) which reacts with hydrazine in accordance with the equation

$$\begin{matrix} CH\cdot COPh \\ \| \\ Ph\cdot C\cdot COPh \end{matrix} + N_2H_4 = \begin{matrix} CH{:}CPh\cdot N \\ | \quad\quad \| \\ Ph\cdot C{:}CPh\text{---}N \end{matrix}$$

and (2) the *trans*-configuration to the isomeride (β), m. p. 123—124°, which is obtained by the action of light and reacts with hydrazine thus:

$$\begin{matrix} CH\cdot Bz \\ \| \\ Bz\cdot C\cdot Ph \end{matrix} + N_2H_4 = \underset{\text{(I.)}}{\begin{matrix} CH\cdot CPh{:}N\cdot NH_2 \\ \| \\ Bz\cdot C\cdot Ph \end{matrix}} \text{ or } \underset{\text{(II.)}}{\begin{matrix} \quad\quad\quad CH\cdot Bz \\ NH_2\cdot N{:}CPh\cdot \| \\ \quad\quad\quad CPh \end{matrix}}$$

Since, with the *trans*-isomeride, closure of the ring is not effected even by prolonged heating, it is probable that, as soon as it is formed, compound I or II gives rise, by simple transposition of the hydrogen atom of the group, $-CH-$, to a nitrogenated ring compound,

$$CPhBz\begin{matrix} \diagup CH_2\cdot CPh \\ \diagdown NH\cdot N \end{matrix} \quad \text{or} \quad CPh\begin{matrix} \diagup N\text{---}NH \\ \diagdown CHPh\cdot CHBz \end{matrix}$$

In the case of stereoisomerides, the action of light usually effects the conversion of the α-form with the higher melting point into the

β-form with the lower melting point, the α-form generally being the stable or *trans*-, and the β-form the labile or *cis*-modification. Several deviations from this general rule have been observed, and the case now considered furnishes another exception, if the assumption that the *cis*- and *trans*-forms are respectively labile and stable is correct.

T. H. P.

Separation of β-Sulphonic and 2 : 6- and 2 : 7-Disulphonic Acids of Anthraquinone. M. L. CROSSLEY (*J. Amer. Chem. Soc.*, 1915, **37**, 2178—2181).—On attempting to separate the products of the direct sulphonation of anthraquinone by means of their calcium salts, it was found that a large part of the β-sulphonic and 2 : 6-disulphonic acids is precipitated and lost in the calcium sulphate. Experiments have shown that the best yields are obtained by neutralising the sulphonation product with sodium hydroxide and separating the acids in the form of their sodium salts. By carefully concentrating the solution of the sodium sulphonates, the β-sulphonate and the 2 : 6-disulphonate can be separated together, leaving the sodium sulphate and the 2 : 7-disulphonate in solution, from which the former can be precipitated by alcohol. After removing the sodium sulphate by filtration and evaporating the filtrate to dryness, the 2 : 7-disulphonate is obtained as a residue. The β-sulphonate and 2 : 6-disulphonate can be separated by taking advantage of their different solubilities in water; the former separates best from slightly acid solutions. Sodium anthraquinone-2 : 6-disulphonate is very sensitive to sunlight, changing from a light plum colour to nearly black.

In the course of this work a new *substance* was isolated in the form of red needles; this compound, when suspended in alcohol and exposed to sunlight, changes into an unstable green product.

E. G.

Action of Esters on Magnesium Alkyl Iodides. G. L. STADNIKOV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1113—1121. Compare A., 1914, i, 954; this vol., i, 372).—The author has made further applications of his method of preparing esters corresponding with alcohols of high molecular weight, the procedure being as follows: magnesium methyl or ethyl iodide, prepared under Grignard's conditions, is decomposed by the alcohol of the required ester, the mixture being cooled with ice water. The magnesium alkyl iodide thus obtained is heated on a bath to the boiling point of the ether with the methyl or ethyl ester of the acid of the required ester. The product of this reaction is decomposed in the cold with dilute sulphuric acid, the ethereal extract being then washed and dried and the ester fractionated after removal of the solvent. The use of magnesium alkyl bromides should give better results than the corresponding iodides. The latter give rise in nearly all cases to iodides of high boiling points, which decompose on distillation and give an ester coloured with iodine. Removal of these iodides may be effected by exposure of the ethereal solution of the ester to the light for from seven to ten days, accompanied by periodical washing with alkaline water; in some instances, two distillations of the ester with finely divided copper (Naturkupfer C) are sufficient.

The results obtained show that this method is most satisfactory with acids, the anhydrides and chloro-anhydrides of which are not readily accessible (compare Houben, A., 1906, i, 520). It is found, further, that the more phenolic in character the alcohol used becomes, the less completely will its radicle replace that of the ethyl ester; magnesium phenyl iodide itself does not react with ethyl acetate. When the masses of the radicles taking part in the reaction approach equality, the more positive one, even when of lower mass, displaces the other from the ester. The molecular weight of the acid also exerts an influence on the replacement of one radicle by another; thus, replacement of the ethyl of ethyl benzoate by menthyl proceeds slowly and the yield of menthyl ester, even on prolonged heating, does not reach the yields obtained in the case of acetic and propionic esters.

Although amides react with alcohols, forming esters and ammonia or amines, and acetamide reacts with sodium ethoxide, giving ethylamine, the amides do not react with magnesium alkyl iodides.

Menthyl acetate, prepared from magnesium menthyl iodide and ethyl acetate, was obtained in 93% yield, menthyl propionate in 80% yield, and menthyl benzoate in 64·6% yield. *Menthyl iminoacetate*, $C_{24}H_{43}O_4N$, has m. p. 48—50°, b. p. 263°/14 mm. *Menthyl nitrilotriacetate*, $C_{36}H_{63}O_6N$, forms slender needles, m. p. 80—81°, and was obtained in 88% yield. In the interaction of ethyl acetate or butyrate with the magnesium derivative of terpineol, the whole of the latter undergoes dehydration, forming a hydrocarbon, $C_{10}H_{16}$, b. p. 182—184°/760 mm. Menthyl benzoate and magnesium benzhydryl iodide do not interact, but benzhydryl acetate reacts with magnesium menthyl iodide, yielding benzhydrol. The iodomagnesium derivative of methylaniline reacts neither with ethyl acetate nor with benzamide. T. H. P.

New Halogen Derivatives of Camphor. Part I. α′-Chlorocamphor; with a Note on Isomerism, Static and Dynamic. THOMAS MARTIN LOWRY and VICTOR STEELE (T., 1915, **107**, 1382—1396).—The existence of two series of ortho-derivatives of camphor has long been known (Marsh, T., 1890, **57**, 828; Lowry, T., 1898, **73**, 569; Haller and Minguin, A., 1901, i, 599; Forster, T., 1902, **81**, 160; Kipping, P., 1905, **21**, 125) but, unlike the α-derivatives, which are generally stable, the α′-derivatives have in no case hitherto been isolated, although it has been possible to predict the specific rotatory power of certain of them (Lowry, T., 1906, **89**, 1033).

α′-Chlorocamphor has now been obtained pure in the following manner. The amount of α′-chlorocamphor produced by the action of alkali on the α-isomeride in hot alcoholic solution amounts to approximately 12%; after this equilibrium is attained, the solution is acidified with dilute hydrochloric acid and cooled to −18°, when much of the unaltered α-isomeride separates; the α′-chlorocamphor remains entirely in solution and can be isolated in a crude condition by evaporation. Further purification can be effected by dissolving in alcohol and cooling to −18°, when part of the admixed α-isomeride crystallises; by recovering the dissolved solid from the mother liquor and repeating the process several times, the α-isomeride can finally be

obtained pure. *α′-Chlorocamphor* is a soft, camphor-like substance, feathery crystals, m. p. 117°, $[\alpha]_D$ +35°; the specific rotation was also determined for other wave-lengths. In alcoholic solution, the addition of a small quantity of sodium ethoxide causes rapid isomerisation; if the solution is a concentrated one, α-chlorocamphor then separates, but in more dilute solution a mixture of the α- and α′-isomerides is obtained in the same proportions as in that resulting from a solution of the α-isomeride under the same conditions. Bromination of α and α′-chlorocamphors gives rise to the same isomorphous mixture of α′-chloro-α-bromocamphor and α-chloro-α′-bromocamphor, a result which affords strong confirmation of the theory of Lapworth (T., 1904, **85**, 30) as to the activity of the enol form in the replacement of hydrogen in ketonic compounds by halogens. Nitration, on the other hand, converted the α′-chlorocamphor into α′-chloro-α-nitrocamphor, m. p. 132°, whilst the α-isomeride under similar treatment yields only α-chloro-α′-nitrocamphor (compare Lowry, T., 1898, **73**, 986).

Attention is drawn to the close analogy between the phenomena in the case of the isomerides of "ethyl acetoacetate" and of α- and α′-chlorocamphor. It is suggested that the term "dynamic isomerism" should be applied generally to all cases in which isomerism passes from a static to a dynamic condition; the term "tautomerism" should be restricted in its original sense to such pairs as the 1 : 2- and 1 : 6-di-derivatives of benzene, whilst the term "desmotropy" should cover those cases in which isomerisation is due to a rearrangement of bonds caused by the displacement of a hydrogen atom. D. F. T.

Chemical and Physical Properties of Oils Distilled from the Various Parts of the Plant, Acorus Calamus, L. G. A. Russell (*J. Amer. Chem. Soc.*, 1915, **37**, 2387—2394).—An account is given of the examination of *Acorus calamus* cultivated on upland soil at Madison, Wis. The results show that these plants yield less oil than those grown in their natural habitat. The fresh aerial parts of the plant (1) yielded 0·123% of volatile oil; the dried rhizomes (2) 0·638%; and the dried roots (3) 2·50%. A small quantity of air-dried rhizomes (4) from Bell, Md., gave 0·95% of oil, and a commercial sample of dry rhizomes (5) 1·493%.

The various specimens of oil thus obtained furnished the following constants: (1) D^{23} 0·9509; $[\alpha]_D^{23}$ +12·2°; n_D^{23} 1·5035; acid number, 0; ester number, 12·6; acetylation number, 53·05. (2) D^{23} 0·9547; $[\alpha]_D^{23}$ +21·7°; n_D^{23} 1·4990; acid number, 0; ester number, 15·5; acetylation number, 38·40. (3) D^{23} 0·9491; $[\alpha]_D^{23}$ + 18·7°; n_D^{23} 1·5065; acid number, 0; ester number, 23·7; acetylation number, 42·10. (4) D^{23} 0·9938; n_D^{23} 1·5140; acid number (determined eight weeks after distilling), 8·15; ester number, 55·3; saponification number, 63·45. (5) D^{23} 0·9945; n_D^{23} 1·5080; acid number (determined eight weeks after distilling), 5·75; ester number, 42·5; saponification number, 48·25.

Phenols were absent from all the oils. Aldehydes were present and in largest amount in the oil from the aerial parts of the plant. All the oils contained combined acids; the oil from the aerial parts yielded butyric and heptoic acids. Fractional distillation of the oils

gave results indicating that the constituents vary to some extent both in character and quantity. E. G.

Butyl Butyrate Occurring in Some Eucalyptus Oils. HENRY G. SMITH (*J. Roy. Soc. New South Wales*, 1914, **48**, 464—468).—The lower boiling fractions of the oil of *Eucalyptus Perriniana* of either New South Wales or Tasmanian origin contain notable quantities of an ester which investigation of the products of saponification has shown to be *n*-butyl butyrate. The saponification number of the crude oil was 52·6, corresponding with 13·5% of this ester. Methyl, ethyl, and propyl alcohols seemed to be entirely absent from the products of saponification. G. F. M.

Phenols Occurring in Some Eucalyptus Oils. ROBERT ROBINSON and HENRY G. SMITH (*J. Roy. Soc. New South Wales*, 1914, **48**, 518—519).—Although phenolic substances rarely occur in the essential oils of the Eucalyptus species, a phenol has been detected in the oils of *E. linearis* and *E. Risdoni*, for which the name *tasmanol* is proposed. It was isolated by extraction with aqueous sodium hydroxide in the usual manner. It boils at 268—273° (uncorr.) and 175°/25 mm. It is optically inactive, and has D^{23} 1·077, and μ 1·5269 at 22°. It gives a deep red coloration with ferric chloride, contains one methoxy-group, and appears to have two hydroxyl groups in the para-position. Another phenol giving a green colour with alcoholic ferric chloride was also detected in the phellandrene-free oils derived from certain species. G. F. M.

Oil of Pistacia Lentiscus. E. SERNAGIOTTO and NERINA VITA (*Ann. Chim. Applicata*, 1915, **4**, 92—93).—When freed from volatile matter by distillation in a current of water apour, this oil has the following constants: D^{15} 0·9188; n_D^{14} 66·00 (Zeiss butyro-refractometer); acid number, 15·92; saponification number, 165·58; saponification number after acetylation, 203·03; Hehner number, 94·824; Maumené number, 46·2; iodine number, 83·61; iodine number of the acids, 85·96. The acids consist of palmitic and oleic acids. The oil contains about 0·5% of optically inactive volatile matter, D^{15} 0·8654, b. p. 165°, bromine number, 285·4, having an odour resembling that of terpenes and giving no solid products with nitrosyl chloride or bromine. T. H. P.

The Chemistry of the Asphalts with Especial Reference to their Photochemical Properties. PAUL GÖDRICH (*Monatsh.*, 1915, **36**, 535—548).—Asphalt can to a slight extent combine with sulphur chloride without becoming insoluble in carbon disulphide. The product is darker and harder than the original natural product and also is more sensitive to light. The chemical action of the sulphur chloride is both substitutive and additive, mainly the former. With a larger proportion of sulphur chloride, the solution of asphalt deposits a black, spongy solid containing about 18% of sulphur, whilst there remains unaffected in solution a constituent of lower sulphur content than the original natural material.

Of several samples of asphalt examined, a Cuban product was most sensitive to light. Although light from any part of the spectrum is capable of rendering asphalt insoluble, it is shown that concurrent contact with oxygen is also necessary; the oxygen may be atmospheric, or may be introduced into the asphalt in the form of a little benzoyl peroxide.

Solutions of asphalt exhibit absorption bands in the blue and yellow portions of the spectrum. D. F. T.

Glucoside of *m*-Hydroxybenzaldehyde. G. Bargellini and R. de Fazi (*Gazzetta*, 1915, **45**, ii, 10—12).—*Tetra-acetogluco-m-hydroxybenzaldehyde*, $CHO\cdot C_6H_4\cdot O\cdot C_6H_7O_5Ac_4$, prepared by the interaction of acetobromoglucose and *m*-hydroxybenzaldehyde in presence of sodium hydroxide (compare Mauthner, A., 1912, i, 574), forms colourless needles, m. p. 105—107°, $[\alpha]_D^{23}$ −43°22′. Hydrolysis of the compound by means of cold, concentrated barium hydroxide solution yields only resinous products, incapable of purification. Comparison of the corresponding gluco-*m*-hydroxybenzaldehyde with salinigrin (compare Jowett, T., 1900, **77**, 707; Jowett and Potter, A., 1902, ii, 686) could not, therefore, be effected. T. H. P.

Physicochemical Studies on the Synthesis of a Chlorophyll Pigment. Albert and Alexandre Mary (*Mon. Sci.*, 1915, [v], **5**, i, 121—128).—The authors are of opinion that chlorophyll is a product of the polymerisation and oxidation of aniline: $6PhNH_2 + 15O = C_{36}H_{30}O_4N + 6H_2O + 5NO$. When nitrous acid is added drop by drop to a very concentrated alcoholic solution of aniline, a white deposit is produced, which becomes rose coloured; then heat is developed, an energetic effervescence ensues, and the deposit becomes green. At the end of the reaction the walls of the vessel are coated with a green or reddish-brown deposit and a dark residue, reddish-brown by transmitted light, is found at the bottom of the vessel. By shaking with benzene, a green, fluorescent solution is obtained, which in the presence of light and air becomes red and yields a brown, resinous precipitate exhibiting the properties of Pringsheim's hypochlorin. When the benzene solution is evaporated in darkness, the walls of the vessel become covered with minute, dichroic crystals, which are claimed by the authors to be synthetic chlorophyll.

If a solution of sodium hydrogen carbonate is added to the reacting mixture when it becomes green, the solution yields all its colouring matter to benzene, but if the addition of the alkali is not sufficiently rapid the solution becomes red or brown or ochreous—the colours of dead leaves. The authors claim that they produce in this manner in a few minutes all the phases of oxidation which chlorophyll in nature requires three seasons to effect.

Similar colour reactions can be produced with natural chlorophyll. White or yellow leaves of *Cichorium endivia* (grown in the dark) are extracted with alcohol at 90°. The yellow extract, by treatment with nitrous acid of suitable concentration, can be changed through rose to green or to red with the evolution of nitrous fumes. Also, a solution of chlorophyll (from *Hedera helix*) in acetic acid is reduced by iron;

the latter is removed by potassium ferrocyanide and the amber filtrate contains reduced chlorophyll, which can be re-oxidised by nitrous acid, the solution becoming green and finally reddish-brown.

As regards its solubility in various solvents, its crystalline character, and its spectrophotometric behaviour, synthetic chlorophyll resembles natural chlorophyll. Also, it exhibits Frémy's reaction; its solution in benzene, after being kept for fifteen hours in contact with hydrochloric acid, is almost entirely decolorised, the acid solution being charged with a greenish-blue pigment (phyllocyanin) and a brown precipitate (phylloxanthin) being formed.

The authors' view of the composition of chlorophyll is entirely at variance with that of Willstätter. They claim that magnesium is not an essential constituent of chlorophyll and that it can be removed without altering the essential characteristics of the pigment. A solution of natural chlorophyll in benzene is repeatedly shaken with an equal volume of aqueous ammonia until the latter ceases to remove magnesium hydroxide; the spectrum of the benzene solution is identical with that of the solution before treatment with ammonia.

The authors state that certain chromogenic bacteria (*Bacterium chlorinum, B. viride, Bacillus virens*) produce green chlorophyll when grown in suitable media. By prolonged keeping of a pure culture of *Bacillus olearius fluorescens* on glycerol broth, a greenish-brown, dichroic pigment is obtained. When *Saccharomyces cerevisiae* is introduced into an aqueous solution of sucrose to which a small quantity of an alcoholic solution of aniline sulphate has been added, the liquid becomes yellowish-green and fluorescent in less than six hours, and at the end of several weeks has changed in colour progressively to brownish-red, the changes being quite similar to those produced by *Bacillus olearius fluorescens* under the conditions mentioned above.

Physical constants and analyses are not given in the paper, the authors relying almost entirely on colour reactions as evidence of the statements recorded. C. S.

Desoxyns as Derivatives of Furan. I. I. Kotjukov (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1087—1093. Compare A., 1914, i, 682).—The condensation of cellulose with chlorobenzene in concentrated sulphuric acid yields a *chlorodesoxyn*, $C_{20}H_{14}O_4(C_6H_4Cl)_2$, which forms a grey, amorphous powder, and, on oxidation with alkaline permanganate, gives *p*-chlorobenzoic acid; the cellulose residue occupies, therefore, the para-position to the chlorine atom. In a similar manner, bromobenzene gives a *bromodesoxyn*, $C_{20}H_{14}O_4(C_6H_4Br)_2$, which is a yellow, amorphous powder turning green in the light, and yields *p*-bromobenzoic acid on oxidation. These results are in agreement with the analytical numbers obtained by Nastukov (A., 1902, i, 362, 747; 1907, i, 413) for phenyldesoxyn, these corresponding with the formula $C_{24}H_{14}O_4Ph_2$. The iodine numbers of the phenyldesoxyns of cellulose, 54·2, and dextrose, 53·0, indicate the presence of one double linking in the molecule.

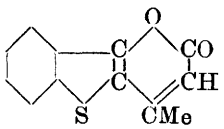
Dry distillation of phenyldesoxyn yields diphenylmethane and a

diphenyldihydrofuran, $C_{16}H_{14}O$, which has the normal molecular weight in freezing benzene, contains one double linking in the molecule, and undergoes gradual decomposition with liberation of benzaldehyde. The conclusion is drawn that desoxyns are derivatives of furan.

T. H. P.

Syntheses of Derivatives of 3-Oxy(1)thionaphthen. Samuel Smiles and Brojendra Nath Ghosh (T., 1915, **107**, 1377—1381).—In extension of the discovery that solutions of certain aromatic mercaptans and disulphides in sulphuric acid behave as if they contain the corresponding sulphonic acids (T., 1910, **97**, 1290; 1911, **99**, 640; 1912, **101**, 572), the authors have further examined the condensation of *o*-thiolbenzoic acid and ethyl acetoacetate in this solvent, and have also investigated the behaviour of dibenzoylmethane and benzoylacetone towards a sulphuric acid solution of *o*-thiolbenzoic acid.

In the condensation of ethyl acetoacetate with *o*-thiolbenzoic acid in the presence of sulphuric acid, the products vary with the conditions, the chief product at 50—60° with equimolecular proportions of the two reagents being 3-oxy(1)thionaphthen, whilst above 70° this product undergoes change into "thioindigo." Unless extreme conditions of dilution are adopted or excess of *o*-thiolbenzoic acid is used, *methyl*-(1)*thionaphthacoumarin* (annexed formula), pale buff coloured prisms, m. p. 164—165°, is also obtained, and indeed constitutes the main product if excess of the ester is used.



Acetylacetone undergoes condensation with *o*-thiolbenzoic acid in sulphuric acid, giving oxythionaphthen. In this case and in that of the condensation with ethyl malonate or acetoacetate the intermediate carbethoxy- or acetyl derivatives, which might be expected, could not be isolated. Dibenzoylmethane, however, reacts with a suspension of *o*-thiolbenzoic acid in sulphuric acid at 50°, giving 2 : 2-*dibenzoyl*-3-*oxy*-(1)*thionaphthen*, $C_6H_4<^{CO}_{S}>CBz_2$, orange-brown needles, m. p. 79°, whilst benzoylacetone yields 2-*benzoyl*-3-*oxy*(1)*thionaphthen*,

$$C_6H_4<^{CO}_{S}>CHBz,$$

dark orange needles, m. p. 115°, which is readily attacked by sulphuric acid at 75°, giving "thioindigo."

Condensation can also be effected in this manner between *o*-thiolbenzoic acid and such substances as ethyl methylacetoacetate, acetonedicarboxylic acid, and ethyl oxaloacetate, but the course of the reaction is less simple; thus the last compound gives rise to a *substance* of uncertain nature, orange needles, m. p. 186—187° (decomp.).

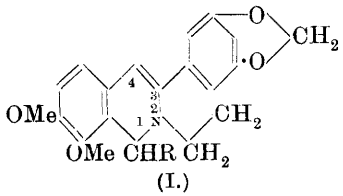
D. F. T.

Arecolidine. Hermann Emde (*Chem. Zentr.*, 1915, i, 1381; from *Apoth.-Zeit.*, 1915, **30**, 240—241).—The mother liquors obtained in the technical preparation of arecoline hydrobromide contain minute

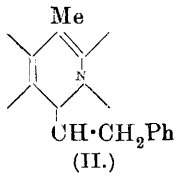
quantities of an isomeric alkaloid which is precipitated by even weak bases. This is designated *arecolidine*, and is probably 3 : 4-*dimethoxy*-1-*methyl*-1 : 2-*dihydropyridine*, $C_8H_{13}O_2N$. It crystallises in transparent needles, m. p. after sublimation 110°, has an odour of acacia, and is very hygroscopic. The *hydrochloride*, $1H_2O$, *hydrobromide*, decomp. 268—271°, *aurichloride*, yellow leaflets, m. p. 219—220° (decomp.), *platinichloride*, stout, dark orange needles, decomp. 222—223°, *methiodide*, clear prisms, decomp. 264°, and the *aurichloride* of the methylated base, $C_9H_{16}O_2NCl_4Au$, m. p. 252° (decomp.) were prepared. The base is unchanged under the conditions in which arecoline is hydrolysed to arecaidine, and therefore the oxygen atoms are not present as a carboxyl group. J. C. W.

Berberine. II. Martin Freund and Karl Fleischer [With Heinrich Herminghaus and Paul Walbaum] (*Annalen*, 1915, **409**, 188—267. Compare A., 1913, i, 502).—Dihydroberberine reacts with methyl iodide at 45—50° to form, in addition to the normal methiodide, decomp. 223—224° (Gadamer [A., 1911, i, 152] gives m. p. 205°), the *hydriodide*, needles, decomp. 205—206°, of a methylated base, which yields two isomeric reduction products. If the methylated base had a constitution analogous to either of those suggested for de-benzyl-*N*-methyldihydroberberine (A., 1913, i, 503), the hydriodide of which is produced in a similar manner from benzyldihydroberberine and methyl iodide, it should yield only one reduction product. Consequently the authors are convinced that both of the constitutions previously suggested for de-benzyl-*N*-methyldihydroberberine are incorrect, and all the more so since an estimation by the Zeisel-Herzig method fails to detect the presence of a NMe group.

Since it has been shown (*loc. cit.*) that the hydrogen atom in position 4 in alkyldihydroberberines (I) is very reactive, it is possible that methyl iodide attacks benzyldihydroberberine at this point and that the substance, m. p. 187—188°, previously called de-benzyl-N-methyldihydroberberine may be 1-benzyl-4-methyldihydroberberine (II), hydrogen iodide being eliminated. This can actually be proved



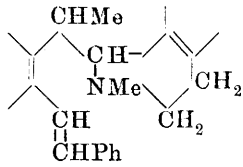
(I.)



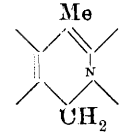
(II.)

(see below). The two reduction products previously described are now shown to be stereoisomeric and their names are to be altered from α- and β-hydro-de-benzyl-*N*-methyldihydroberberine to 1-*benzyl*-4-*methyltetrahydroberberine* (m. p. 162—164°) and ψ-1-*benzyl*-4-*methyltetrahydroberberine* (m. p. 134—136°) respectively. Only the ψ-base forms a methiodide (which has now been obtained indistinctly crystalline, m. p. 245°), by the de-iodination and fission of which is obtained de-1-benzyl-*N*:4-dimethyltetrahydroberberine (formerly named

β-hydro-de-benzyl-*NN*-dimethyldihydroberberine) (III). By oxidation with sodium dichromate and acetic acid, the latter yields hydrastinine and a non-nitrogenous *substance*, crystalline powder, m. p.



(III.)

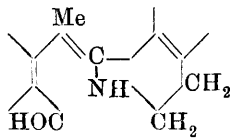


(IV.)

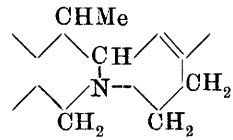
168—171°, of unknown composition. Since in this method of converting benzyldihydroberberine into hydrastinine methyl iodide has been used twice whereas the resulting hydrastinine only contains one methyl group attached to nitrogen, it follows that in the first treatment of benzyldihydroberberine with methyl iodide the methyl group does not become attached to the nitrogen atom; the most probable point of attack is the hydrogen atom in position 4, as stated above.

De-1-benzyl-*N*:4-dimethyltetrahydroberberine methiodide, by successive treatment with silver oxide and alkali, yields a *de-base*, the *methiodide* of which is converted by de-iodination and fission into trimethylamine and the non-nitrogenous compound previously described (A., 1913, i, 504).

Confirmation of the formulæ given above is obtained by the investigation of dihydroberberine. The methylated base, the hydriodide of which is obtained by the action of methyl iodide on dihydroberberine, is 4-*methyldihydroberberine* (IV.), yellow prisms, m. p. 121—122°, darkening at 115°. 4-*Ethyldihydroberberine*, prepared in a similar manner, forms pale yellow, prismatic plates, m. p. 194—195°, darkening at 160°. 4-Methyldihydroberberine does not contain a methylimino-group, and its constitution is proved by its oxidation by alcoholic iodine to 4-*methylberberine hydriodide*, $C_{21}H_{20}O_4NI$, intensely yellow needles, decomp. 244°, darkening at 200°. This salt reacts with magnesium benzyl chloride to form 1-benzyl-4-methyldihydroberberine, identical with that described above, and, after conversion into the *hydrochloride*, $C_{21}H_{20}O_4NCl,H_2O$, yellow plates, decomp. 190°, is changed by alkalis into 4-*methylberberinal* (V.), a yellow, amorphous substance, decomp. above 190°, the hydriodide of which is identical with 4-methylberberine hydriodide and the *cyanide*, $C_{22}H_{20}O_4N_2,H_2O$, prepared from the hydrochloride and aqueous sodium cyanide, forms indistinct crystals, m. p. 164—165°.



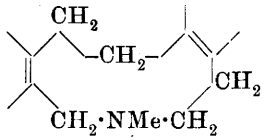
(V.)



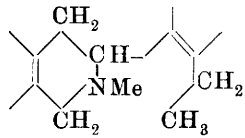
(VI.)

4-Methyldihydroberberine is reduced by hot hydrochloric acid, alcohol, and stannous chloride to 4-*methyltetrahydroberberine* (VI.), colourless, elongated prisms, m. p. 211—212°. By electrolytic reduc-

tion at 20—30° at a lead cathode in 96% alcohol and 30% sulphuric acid, the current density being 0·075 amp./cm.^{2}, it yields in addition a stereoisomeric base, *ψ-4-methyltetrahydroberberine*, long plates, m. p. 110—112°. Pyman's A- and B-de-*N*-methyltetrahydroberberines (T., 1913, **103**, 817) are reduced, the former electrolytically, the latter by hydrogen and colloidal palladium, to A-*hydro-de*-N-*methyltetrahydroberberine* (VII.), prismatic plates, m. p. 127—129°, and B-*hydro-de*-N-*methyltetrahydroberberine* (VIII.), colourless needles, m. p. 102—102·5°, respectively. Neither Pyman's A-base nor its reduc-



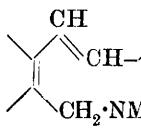
(VII.)



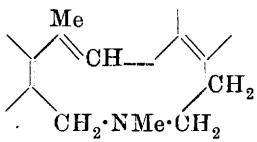
(VIII.)

tion product is identical with 4-methyltetrahydroberberine or its ψ-isomeride.

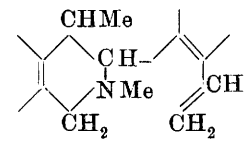
B-*De*-N-*methyltetrahydroberberine methiodide*, colourless or faintly yellow needles, decomp. 228°, is converted by successive treatment with silver oxide and alkali hydroxide into a *base*, $C_{21}H_{25}O_4N$, colourless needles, m. p. 97·5°, called B-*de*-NN-*dimethyltetrahydroberberine* and having formula IX. This is compared with the bases, $C_{22}H_{25}O_4N$, obtained from *4-methyltetrahydroberberine methiodide*, faintly yellow plates, decomp. 247°, and *ψ-4-methyltetrahydroberberine methiodide*, decomp. 267—268°, in a similar manner. These yield respectively *de*-N : 4-*dimethyltetrahydroberberine*, colourless prisms, m. p. 160—162° (*methiodide*, colourless needles, m. p. 200°, which does not yield an amine by successive de-iodination and decomposition by alkali), and *ψ-de*-N : 4-*dimethyltetrahydroberberine*, colourless prisms, m. p. 104—106° (*hydrochloride*, decomp. 241°, colourless prisms). These two isomeric bases can be derived from bases having the formula VI in two ways, their constitutions being represented by X or XI. The latter is the more probable since the



(IX.)



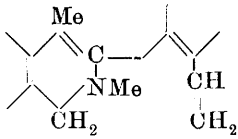
(X.)



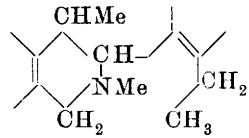
(XI.)

bases are not converted into ammonium bases by warm, dilute alcohol, a change which is common to substances of type X (Gadamer and Voss, A., 1910, i, 415; Freund and Lachmann, A., 1913, i, 507; Pyman, *loc. cit.*). It is noteworthy that the two bases are different, whereas methiodides of two stereoisomeric 1-alkyltetrahydroberberines always yield the same de-1-alkyl-*N*-methyltetrahydroberberine. The two bases are nearly related to *de*-N : 4-*dimethyldihydroberberine* (XII), decomp. about 100° (*hydriodide*, pale yellow crystalline powder, decomp.

208—209°; *methiodide*, crystals, decomp. 143°), obtained by the decomposition of 4-*methyldihydroberberine methiodide*, pale yellow



(XII.)



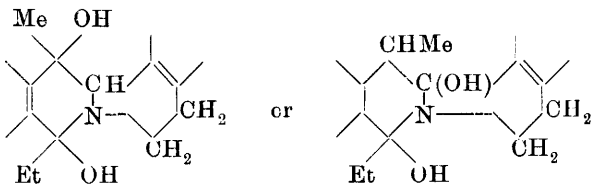
(XIII.)

prisms, decomp. 157—158°. By reduction at a lead cathode de-*N*:-4-dimethyldihydroberberine yields *tetrahydro-de*-N : 4-*dimethyldihydroberberine* (XIII), an oily base which forms a *hydrochloride*, $C_{22}H_{27}O_4N,HCl$, colourless crystals, decomp. 235°.

By electrolytic reduction at a lead cathode in aqueous alcohol and sulphuric acid, and subsequent basification with ammonia, berberine sulphate is converted into tetrahydroberberine, 4-methylberberine hydrochloride into 4-methyltetrahydroberberine and its ψ-isomeride, dihydroberberine methiodide into tetrahydroberberine methiodide (using potassium iodide instead of ammonia), and de-*N*-ethyltetrahydroberberine (prepared from tetrahydroberberine ethiodide, decomp. 243° [Gadamer gives 228—229°]), into *hydro-de*-N-*ethyltetrahydroberberine*, $C_{22}H_{27}O_4N$, colourless prisms, m. p. 103—105° (*sulphate*, crystals, decomp. 270°).

The behaviour of 1-acetonylberberine with methyl iodide is similar to that of 1-alkyldihydroberberines. The chief product is a *substance*, $C_{24}H_{26}O_5NI$, intensely yellow needles, decomp. 251°, which is stable to ammonia and sodium carbonate, but not to alkali hydroxides, and is regarded as 1-*acetonyl*-4-*methyldihydroberberine hydriodide*, since by reduction with stannous chloride, alcohol, and hydrochloric acid it loses the acetonyl group and is converted into 4-methyltetrahydroberberine.

The oxidation of 4-methyl-1-ethyl (propyl, *iso*propyl, and benzyl)-dihydroberberines, previously described under the name de-alkyl-*N*-methyldihydroberberine, has been investigated. The oxidation of the first substance by sodium dichromate and acetic acid, examined by Freund and Commessmann (A., 1913, i, 506), yielded a product, $C_{23}H_{27}O_6N$, to which a satisfactory constitution could not be ascribed by these investigators or by the authors (A., 1913, i, 502). In the light of the new formulæ now advanced, its constitution, deduced from that of 4-methyl-1-ethyldihydroberberine, is represented by XIV and its former name, oxy-de-*N*-methylethyldihydroberberine hydrate, is to be replaced by 4-*methyl*-1-*ethylberberinal hydrate*.

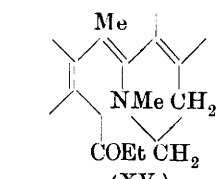


(XIV.)

The substance, which shows many analogies to the similarly constituted hydrastinine and cotarnine, forms a *hydriodide*, small plates, m. p. 221° with previous decomposition, loses 1 mol. of water by treatment with acids, forming yellow salts which are only decomposed by alkali hydroxides, and reacts in acetic acid with potassium cyanide to form 1-*cyano*-4-*hydroxy*-4-*methyl*-1-*ethyltetrahydroberberine*, $C_{24}H_{26}O_5N_2$, crystals, m. p. 220° (decomp.); it also reacts with methyl alcohol to form 4-*hydroxy*-1-*methoxy*-4-*methyl*-1-*ethyltetrahydroberberine*, $C_{24}H_{29}O_6N$, faintly yellow needles, m. p. 115°. The last two compounds are decomposed by hydrochloric acid, losing hydrogen cyanide and methyl alcohol respectively, and yielding the yellow hydrochloride. The electrolytic reduction of 4-methyl-1-ethylberberinal hydrate at a lead cathode in alcohol and dilute sulphuric acid yields 4-methyl-1-ethyltetrahydroberberine and its ψ-isomeride. The re-oxidation of these to 4-methyl-1-ethyltetrahydroberberinal hydrate (Freund and Commessmann, *loc. cit.*, old names) is readily explicable by the new formulæ.

By careful fusion, or by boiling with concentrated potassium hydroxide, 4-methyl-1-ethylberberinal hydrate loses $2H_2O$, and is converted into a *substance*, $C_{23}H_{25}O_4N$, yellow pyramids, m. p. 185—186°, which is regarded as 4-*methyl*-1-*ethylidenedihydroberberine*. The salts of this are normally constituted, and are only decomposed by alkali hydroxides; the *hydrochloride*, yellow needles, has m. p. 195—196°, with previous decomposition, and the *hydriodide*, which can also be prepared by heating 4-methyl-1-ethylberberinal hydrate with an excess of methyl iodide at 100°, forms yellow needles, m. p. 220°, with previous decomposition.

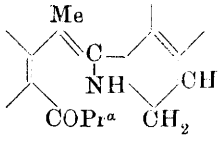
By prolonged heating with an excess of methyl iodide at 100°, 4-methyl-1-ethylidenedihydroberberine yields a *methiodide*, $C_{24}H_{26}O_4NI$, small plates, decomp. 230°, m. p. 235°, which forms a neutral solution (alcoholic) by treatment with silver oxide and is converted by aqueous alcoholic sodium hydroxide into a neutral substance which is regarded as *N*: 4-*dimethyl*-1-*ethylberberinal* (XV); it forms a *methochloride* slender needles, m. p. 200—201°, by solution in hydrochloric acid, and regenerates 4-methyl-1-ethylidenedihydroberberine methiodide by treatment with acetic acid and potassium iodide.



(XV.)

1-*n*-Propyldihydroberberine and methyl iodide react at 100° to form as chief product the *hydriodide*, citron yellow crystals, decomp. 224—227°, of 4-*methyl*-1-n-*propyldihydroberberine*, $C_{24}H_{27}O_4N$, irregular leaflets, m. p. 129—131°. This base, by oxidation with acetic acid and sodium dichromate and subsequent treatment with potassium cyanide, yields the ψ-*cyanide*, colourless, rectangular plates containing Et·OH, decomp. 194°, of 4-*methyl*-1-n-*propylberberinal hydrate*, $C_{24}H_{29}O_6N$, faintly yellow crystals, m. p. 121—123° (decomp.). This oxidation product forms a *hydriodide*, decomp. 208°, *nitrate*, colourless, rectangular leaflets, decomp. 214°, and *sulphate*, colourless needles, and behaves similarly to the ethyl homologue except that by fusion or by boiling with concentrated alkali it loses only $1H_2O$ and

yields 4-*methyl*-1-n-*propylberberinal* (annexed formula), yellow crystals, m. p. 194 (*hydriodide*, yellow leaflets, decomp. 214°, *sulphate*, yellow prisms, decomp. 229°).



In the preparation of de-1-benzyl-*N*-methyltetrahydroberberine from 1-benzyltetrahydroberberine methiodide (Freund and Fleischer, *loc. cit.*) a by-product has now been isolated, which is isomeric with de-1-benzyl-*N*-methyltetrahydroberberine and is called allo-*de*-1-*benzyl*-N-*methyltetrahydroberberine*. It crystallises in colourless plates, m. p. 138—140°, forms a *methiodide*, grey, crystalline powder, decomp. 197°, does not yield hydrastinine by oxidation, and yields allo-*hydro*-*de*-1-*benzyl*-N-*methyltetrahydroberberine*, $C_{28}H_{31}O_4N$, colourless prisms, m. p. 156—157°, by reduction with hydrogen and colloidal palladium.

Two sections of the paper deal with the stereoisomerism and the nomenclature of berberine derivatives. C. S.

The Alkaloids of the Calabar Bean. III. Action of Sulphur Dioxide on Eserine, Geneserine, and their Derivatives. Max Polonovski and Charles Nitzberg (*Bull. Soc. Chim.*, 1915, [iv], **17**, 290—297).—A more detailed account of work already published (compare this vol., i, 892). The authors have isolated a *sulphonated* derivative of eseroline, $C_{13}H_{17}ON_2\cdot SO_3H,2H_2O$, m. p. 235°; $[\alpha]_D$ – 100°. W. G.

Condensation of Ethyl Acetonedicarboxylate with Aldehydes, Ammonia, and Amines. P. Petrenko-Kritschenko (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1126—1132).—*Ethyl* 2 : 6-*diiso*-*propyl*-4-*piperidone*-3 : 5-*dicarboxylate*, $NH<\begin{matrix}CHPr^{\beta}\cdot CH(CO_2Et)\\ CHPr^{\beta}\cdot CH(CO_2Et)\end{matrix}>CO$, obtained by the interaction of ethyl acetonedicarboxylate, *iso*butaldehyde, and ammonia, forms crystals, m. p. 57°, and gives a red coloration with ferric chloride in alcoholic solution. Its *platinichloride*, and its *nitrite*, $C_{17}H_{29}O_5N,HNO_2$, m. p. 106°, which gives Liebermann's reaction, were prepared. When oxidised with chromic oxide, γ-piperidones with phenyl side-groups readily yield the corresponding pyridone derivatives; the present compound yields only a very small proportion of a substance, m. p. 243°, which is probably of pyridonic structure.

The *compound*, $CO[CH(CO_2Et)\cdot CHPh\cdot NH\cdot CH_2Ph]_2$, obtained by the interaction of ethyl acetonedicarboxylate (1 mol.), benzaldehyde (2 mols.), and benzylamine (2 mols.) in cooled benzene solution, forms crystals, m. p. 122—124°. Attempts to purify this compound by crystallisation from alcohol resulted in the formation of *ethyl* 2 : 6-*diphenyl*-1-*benzylpiperidone*-3 : 5-*dicarboxylate*,

$$CH_2Ph\cdot N<\begin{matrix}CHPh\cdot CH(CO_2Et)\\ CHPh\cdot CH(CO_2Et)\end{matrix}>CO,$$

which forms crystals of the rhombic system, m. p. 90°, and is, in some cases, accompanied by a *compound*, m. p. 220—230°, which was not investigated.

The *triamino*-compound, $NH{:}C[CH(CO_2Et)\cdot CHPh\cdot NH_2]_2$ or $NH_2\cdot CHPh\cdot CH(CO_2Et)\cdot C(NH_2){:}C(CO_2Et)\cdot CHPh\cdot NH_2$, formed as a by-product in the condensation of ethyl acetonedicarboxylate, benzaldehyde, and ammonia (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 299), forms crystals, m. p. 160°. When treated with hydrochloric acid, it is converted into the *diamino*-compound, $CO[CH(CO_2Et)\cdot CHPh\cdot NH_2]_2$, m. p. 112°, which gives a red coloration with ferric chloride in alcoholic solution. T. H. P.

Formyl and Aldehydic Derivatives of Pyrroles and Indoles. Luigi Alessandri (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 194—199).—The method described by Tschelincev and Terentjev (this vol., i, 452) for the preparation of pyrrole-2-aldehyde had been given earlier by the author (this vol., i, 452).

Since many of the reactions common to the true aldehydes, such as the formation of hydroxamic acids, fail with pyrrole-2-aldehyde, although they are given by 1-methylpyrrole-2-aldehyde, Angeli and Alessandri (this vol., i, 454) considered that the former has a hydroxymethylenic structure. 2-Methylindole-3-aldehyde does not yield a hydroxamic acid, and 1 : 2-dimethylindole-3-aldehyde gives only traces of a copper salt, which is coloured violet by ferric chloride; the latter result is regarded as due to the fact that the aldehyde is an orthodisubstituted compound.

The action of potassium hydroxide and chloroform on indole gives only a small yield of indole-3-aldehyde (compare Ellinger, A., 1906, i, 696). Application of the author's method (*loc. cit.*) to 2-methylindole and to indole also results in small yields of the corresponding 3-aldehydes, the principal products of the reactions being respectively a crystalline compound, m. p. 76·5°, and an oil crystallising only at very low temperatures; these products are isomeric with the aldehydes expected, and are evidently 1-formyl-2-methylindole and 1-formylindole.

Similarly, the action of an alkyl formate on the magnesium pyrryl haloid gives: (1) with 2 : 5-dimethylpyrrole: a small proportion of 2 : 5-dimethylpyrrole-3-aldehyde (compare Plancher and Ponti, A., 1910, i, 132), and, in larger yield, 1-*formyl*-2 : 5-*dimethylpyrrole*, $CHO\cdot N<\begin{matrix}CMe{:}CH\\ CMe{:}CH\end{matrix}$, m. p. 35°; (2) with 2 : 4-dimethylpyrrole: a moderately good yield of 2 : 4-*dimethylpyrrole*-5-*aldehyde*, C_7H_9ON, m. p. 89°, which forms an *oxime*, m. p. 131°, and yields 2 : 4-dimethylpyrrole-5-carboxylic acid when oxidised with potassium permanganate in acetone solution. When the dry sodium salts of these two aldehydes are heated in sealed tubes at 100° with methyl iodide (1 mol.), they give the respective methyl derivatives which, from the analogous preparation of 1 : 2-dimethylindole-3-aldehyde (this vol., i, 454), must be regarded as 1-methyl derivatives. In this way, 2 : 5-dimethylpyrrole-3-aldehyde gives, in good yield, a compound, m. p. 96°, which with dihydroxyammonia furnishes, only under special conditions, a cherry-red coloration with ferric chloride; 2 : 4-dimethylpyrrole-5-aldehyde gives a poor yield of an oily methyl derivative, which forms an oxime, m. p. 145°, and reacts only partially with dihydroxyammonia, the product then giving a brick-red coloration with ferric chloride.

From the results described above, it appears probable that the liquid product obtained by Tschelincev and Terentjev (*loc. cit.*) in their preparation of pyrrole-2-aldehyde, and regarded by them as a mixture of unaltered pyrrole and alkyl formate, contains 1-formylpyrrole; its content of nitrogen is, indeed, in almost exact accord with this assumption.

Analysis of the sodium salt of pyrrole-2-aldehyde shows that it is a true salt, and thus confirms the hydroxymethylenic structure of this compound. Pyrrole-2-aldehyde condenses with phenylhydroxylamine, giving the *compound*, $C_4H_4N\cdot CH:NPh:O$, m. p. 120°, which, like other *N*-phenyl ethers of oximes, is unstable towards sunlight.

The instability of the 1-methylpyrrole-2-aldehyde obtained by Fischer (A., 1913, i, 1225) results from the method employed in its preparation. When the dry sodium salt of pyrrole-2-aldehyde is heated at 100° in a sealed tube with methyl iodide, care being taken that the latter remains in slight excess, 1-methylpyrrole-2-aldehyde is obtained as an oil which is moderately stable in the crude state, and, after distillation under reduced pressure, remains unchanged for more than a month. Its *azine*, $C_6H_7N:N\cdot N:C_6H_7N$, m. p. 120°, was prepared. The aldehyde reacts readily with dihydroxyammonia and then gives the characteristic violet-blue coloration with ferric chloride, but the hydroxamic acid was not isolated owing to the paucity of the material available.

By oxidation of 2-methylindole-3-aldehyde by means of permanganate in faintly alkaline aqueous solution, Plancher and Ponti (A., 1907, i, 341) obtained acetylanthranilic acid. When, however, the oxidation is carried out in acetone solution, 2-methylindole-3-carboxylic acid is obtained in good yield, and the author regards this procedure as more generally applicable to the conversion of aldehydes into the corresponding carboxylic acids.

The action of ethyl nitrate on magnesium 2-methylindolyl iodide furnishes 3-nitro-2-methylindole (compare Angeli and Angelico, A., 1901, i, 45; Angelico and Velardi, A., 1904, i, 526) in good yield, possibly together with a 1-substituted derivative. T. H. P.

Some Derivatives of Pyrrole. II. G. Karl Almström (*Annalen*, 1915, **409**, 291—305. Compare A., 1913, i, 1240).—Benzoylacetone and phenacylaniline condense in boiling glacial acetic acid to form a *substance*, $C_{24}H_{19}ON$, sulphur-yellow crystals, m. p. 155—156°, which has, of the four possible formulæ, the constitution $NPh<\begin{matrix}CMe:CBz\\ CH=CPh\end{matrix}$, and is therefore 4-*benzoyl*-1 : 3-*diphenyl*-5-*methylpyrrole*. This is proved by the fact that on hydrolysis with moderately concentrated sulphuric acid it yields benzoic acid and 1 : 3-*diphenyl*-5-*methylpyrrole*, almost colourless, rhombic plates, m. p. 68—69°. The benzoyl group of the benzoic acid is that originally present in the benzoylacetone, because when 4-*benzoyl*-1-*phenyl*-3-p-*tolyl*-5-*methylpyrrole*, faintly yellow crystals, m. p. 138—139°, prepared by condensing benzoylacetone and *p*-tolacylaniline, is hydrolysed in a similar manner, it yields benzoic acid and 1-*phenyl*-3-p-*tolyl*-5-*methylpyrrole*, almost colourless needles, m. p. 108—109°. In a similar

manner, acetylacetone condenses with phenacylaniline and with *p*-tolacylaniline to form respectively 4-*acetyl*-1 : 3-*diphenyl*-5-*methylpyrrole*, straw-yellow plates, m. p. 104—105°, and 4-*acetyl*-1-*phenyl*-3-p-*tolyl*-5-*methylpyrrole*, faintly yellow needles, m. p. 110—111°, each of which is hydrolysed by sulphuric acid, yielding acetic acid and, the former 1 : 3-diphenyl-5-methylpyrrole, the latter 1-phenyl-3-*p*-tolyl-5-methylpyrrole.

4-Acetyl-1 : 3-diphenyl-5-methylpyrrole reacts readily with benzaldehyde in boiling alcoholic sodium hydroxide to form 4-*cinnamoyl*-1 : 3-*diphenyl*-5-*methylpyrrole*, yellow plates, m. p. 148—149°.

Phenacylmethylamine hydrobromide is best prepared by treating ω-bromoacetophenone in ether with alcoholic 33% methylamine, and treating the filtered and washed ethereal solution with 40% hydrobromic acid; by evaporating the acid solution, a brominated by-product, m. p. 134°, and phenacylmethylamine hydrobromide are obtained. The latter reacts with acetylacetone in boiling glacial acetic acid containing sodium acetate to form 4-*acetyl*-3-*phenyl*-1 : 5-*dimethylpyrrole*, faintly yellow prisms, m. p. 67—68°, which yields 4-*cinnamoyl*-3-*phenyl*-1 : 5-*dimethylpyrrole*, needles, m. p. 107—108°, by treatment with benzaldehyde and boiling alcoholic sodium hydroxide.

By the reaction between acetylacetone, phenacylamine hydrochloride, and sodium acetate in 75% acetic acid on the water-bath Knorr and Lange in 1902 obtained 4-acetyl-3-phenyl-5-methylpyrrole; a second, more soluble product is 2-*benzoyl*-3 : 5-*dimethylpyrrole*, rectangular plates, m. p. 118—119°.

By boiling with acetic anhydride containing a drop of concentrated sulphuric acid, 4-benzoyl-1 : 3-diphenyl-5-methylpyrrole yields 4-*benzoyl*-2-*acetyl*-1 : 3-*diphenyl*-5-*methylpyrrole*, colourless plates, m. p. 133—134°, which is converted into 4-*benzoyl*-2-*cinnamoyl*-1 : 3-*diphenyl*-5-*methylpyrrole*, straw-yellow needles, m. p. 149—150°, by benzaldehyde and boiling alcoholic sodium hydroxide, 1 : 3-diphenyl-5-methylpyrrole yields 2 : 4-*diacetyl*-1 : 3-*diphenyl*-5-*methylpyrrole*, colourless plates, m. p. 85—86°, which can be converted into 2 : 4-*dicinnamoyl*-1 : 3-*diphenyl*-5-*methylpyrrole*, pale yellow needles, m. p. 170—171°, and 4-acetyl-3-phenyl-5-methylpyrrole yields 1(*or* 2) : 4-*diacetyl*-3-*phenyl*-5-*methylpyrrole*, colourless crystals, m. p. 182—183°. C. S.

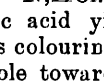
Preparation of Diphenyldipyrrylmethane, Diphenylpyrrylcarbinol, and a New Colouring Matter of the Pyrrole Series. V. V. Tschelincev, B. V. Tronov, and A. P. Terentéev (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1211—1223).—The condensation of benzophenone with pyrrole in alcoholic solution, and in presence of a small proportion of hydrochloric acid as catalyst, yields (1) diphenyldi-2-pyrrylmethane (compare Khotinsky and Patzewitch, A., 1909, i, 830), and (2) diphenyl-2-pyrrylcarbinol, which appears to be the first product of the reaction, and gives rise to diphenyldi-2-pyrrylmethane by interaction with a second molecule of pyrrole. It has been previously shown that the action of esters on magnesium pyrryl bromide gives products in which the 2-hydrogen of the pyrrole ring is substituted (this vol., i, 470), and the fact that the diphenylpyrrylcarbinol obtained from benzophenone and pyrrole is also formed, along with

diphenyldi-2-pyrrylmethane, by the action of magnesium pyrryl bromide on benzophenone shows it to be diphenyl-2-pyrrylcarbinol. Removal of the elements of water (1 mol.) from this alcohol results in the formation of a colouring matter,  , which is allied, on the one hand, to the triphenylmethane dyes, and, on the other, to difluorene, fulvene, indigotin, and, possibly, chlorophyll and hæmin; as with malachite-green, the tertiary nitrogen atom of this colouring matter may play the part of an auxochromic group.

Diphenyldi-2-pyrrylmethane, $CPh_2(C_4H_4N)_2$, forms slender, white crystals, m. p. 264°, and exhibits normal cryoscopic behaviour in bromoform.

Diphenyl-2-pyrrylcarbinol, $C_4H_4N\cdot CPh_2\cdot OH$, forms a dark red, amorphous powder, decomposing at about 170°, and is analogous to diphenylthienylcarbinol (compare Thomas, A., 1908, i, 360). It acts as an indicator, being coloured a bright red, resembling magenta, by inorganic or organic acids, and yellow by alkali hydroxide or carbonate or ammonia. In the air it undergoes gradual change, probably owing to anhydrification, and possibly to condensation, the molecular weight in freezing benzene (or bromoform) increasing from 310—321 to 464—474; the red colour of its solution slowly alters to bluish-violet.

Diphenyl-2-pyrrylcarbinol is a coloured base, capable, like triphenylmethane compounds, of conversion into pigments by acids:

$$C_4H_4N\cdot CPh_2\cdot OH + HCl = H_2O + \text{  }$$

Treatment with zinc dust and hydrochloric acid yields the leuco-compound, $C_4H_4N\cdot CHPh_2$. By means of this colouring matter, tissues are dyed raspberry-red, the colour being stable towards the action of boiling water or treatment with soap or bisulphite. T. H. P.

Pyrrole-Black. A. Angeli (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 3—6).—Up to a certain point, the oxidation of pyrrole by means of hydrogen peroxide in acetic acid solution proceeds similarly to the auto-oxidation of this compound (compare Ciamician and Silber, A., 1912, i, 645), a product exhibiting all the properties of succinimide being formed. This is accompanied by a black compound, or possibly mixture of compounds, to which the name *pyrrole-black* is given. In some cases, this compound separates spontaneously as a fine, black powder, and in others the separation may be readily effected by addition of sodium sulphate solution. Pyrrole-black is insoluble in almost all solvents but dissolves readily in alkali and may be reprecipitated by acidification with acetic acid. This compound shows marked resemblance to the melanins; thus, the atomic relation, C : H : N has the value, 5 : 5 : 1, and the products obtained by fusion with potassium hydroxide or by simple heating include pyridine bases, together with vapours which impart an intense red coloration to a pine shaving moistened with hydrochloric acid.

When subjected to the further action of hydrogen peroxide in acetic acid, the black powder passes gradually into solution, the liquid

becoming first orange and then yellow with a faint green fluorescence; this action resembles that of hydrogen peroxide on the melanins of brown or black hair, which becomes blonde. T. H. P.

Nitration of 2-Aminopyridine. II. A. E. TSCHITSCHIBABIN and B. A. RAZORENOV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1286—1296).—It has been shown that 2-aminopyridine is readily nitrated in presence of concentrated sulphuric acid, giving 5-nitro-2-aminopyridine and 3-nitro-2-aminopyridine (this vol., i, 591). Further investigation shows that nitration of 2-aminopyridine is directed, first to the hydrogen of the amino-group, the initial product being pyridyl-2-nitroamine, which undergoes subsequent isomerisation into 3- and 5-nitro-2-aminopyridines. In comparison with the analogous benzenediazoic acid, pyridyl-2-nitroamine exhibits marked stability towards acids, its solution in concentrated sulphuric acid undergoing decomposition slowly at the ordinary temperature and very slowly indeed at temperatures below 0°; in the hot, however, isomerisation occurs readily and yields principally 3-nitro-2-aminopyridine, the proportion of 5-nitro-2-aminopyridine increasing as the temperature of isomerisation rises. Further action of nitric acid on 5-nitro-2-aminopyridine yields 5-nitropyridyl-2-nitroamine, and this undergoes isomerisation, although with more difficulty than pyridyl-2-nitroamine, yielding probably 3 : 5-dinitro-2-aminopyridine.

Another characteristic property of the nitroamines of pyridine is the almost complete loss of the basic properties of the nitrogen of the pyridine nucleus, whereas the acid properties are strongly marked. Certain differences in the external forms of different preparations and in the rates at which they are decomposed by solutions of alkali carbonates are perhaps due to the existence of the isomerides, $C_5H_4N\cdot NH\cdot NO_2$ and $C_5H_4N\cdot N{:}NO\cdot OH$. Reduction of pyridyl-2-nitroamine by zinc dust in alkaline solution yields 2-pyridylhydrazine.

Pyridyl-2-nitroamine, $C_5H_4N\cdot NH\cdot NO_2$, forms almost white needles, decomposing at about 184° with evolution of gas, and dissolves in sodium carbonate solution with liberation of carbon dioxide. Its potassium salt forms nacreous plates or flattened needles.

5-Nitropyridyl-2-nitroamine, $NO_2\cdot C_5H_3N\cdot NH\cdot NO_2$, forms stout plates or flat needles, decomposing when heated.

3 : 5-Dinitro-2-aminopyridine, $C_5H_2N(NO_2)_2\cdot NH_2$, forms long, straw-yellow needles, m. p. 191—192°, and gives slowly a brown coloration with alkalis.

2-Pyridylhydrazine, $C_5H_4N\cdot NH\cdot NH_2$, forms colourless needles, m. p. 46—48°, which are gradually oxidised to a viscous resin; its aqueous solution reduces Fehling's solution and ammoniacal silver oxide solution. With benzaldehyde in acetic acid solution, it yields *benzaldehyde-2-pyridylhydrazone*, $C_{12}H_{11}N_3$, which forms white needles or prisms, m. p. 150—151°. T. H. P.

Formation of γ-Amino-derivatives on Amination of Compounds containing the Pyridine Nucleus. A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 835—838).—That the action of sodamide on pyridine derivatives may yield 4- as well as 2-amino-compounds (compare this vol., i. 590) is shown by heating a mixture

of 2 : 6-dimethylpyridine, toluene, and sodamide, 4-amino-2 : 6-dimethylpyridine being obtained among the products after decomposition by means of water. In this case, however, the reaction takes place with far greater difficulty and gives a poorer yield than when the amino-group enters the 2-position of the pyridine nucleus. That 4-aminopyridine is obtained in small proportion when sodamide acts on pyridine at 120° (*loc. cit.*) has been definitely proved by isolation of its platinichloride. T. H. P.

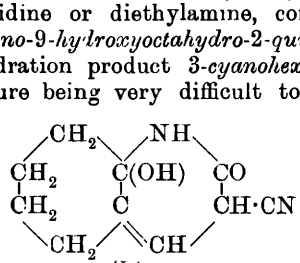
Production of Picrates of Ethylpyridinium and Analogous Bases. R. (FRH.) VON WALTHER (*J. pr. Chem.*, 1915, [ii] **92**, 208; compare this vol., i, 836, and Kohn, *ibid.*).—The author agrees that his work only amplified that of Kohn and Gauer. J. C. W.

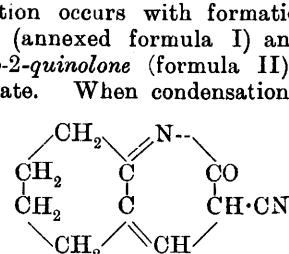
Catalysis in the Synthesis of Homologues of Pyridine by Ladenburg's Method. A. E. TSCHITSCHIBABIN and P. F. RIUMSCHIN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1297—1302).—Benzylpyridine is not formed when the vapours of benzyl chloride and pyridine are passed together through a long glass tube heated at 300°, although in sealed tubes the reaction proceeds well at 270° or even 250° (A., 1901, i, 484). When liquid benzyl chloride and pyridine are heated together in a reflux apparatus, moderately good yields of benzylpyridines are obtained in presence of a little powdered aluminium or magnesium and very good yields when a little powdered copper or cuprous chloride is added.

[With KAZANCEV.] Ethyl iodide and pyridine, when heated in presence of copper, give a mixture of mono- and di-ethylpyridines in good yield. T. H. P.

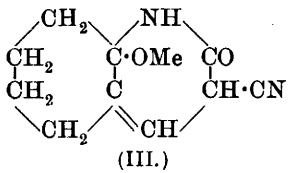
Formation of Heterocyclic Compounds from Cyanoacetamide and Hydroxymethylene Ketones. I. HEMENDRA KUMAR SEN-GUPTA (T., 1915, **107**, 1347—1367).—Hydroxymethylene-ketones have been relatively little applied to synthetical work (compare Errera, A., 1900, i, 33; 1901, i, 43; Simonsen, T., 1908, **93**, 1022). It has now been found that hydroxymethylene-*cyclo*ketones undergo condensation with cyanoacetamide, the products being quinoline derivatives instead of the *iso*quinoline derivatives at first expected.

When an aqueous solution of cyanoacetamide is mixed with an alcoholic solution of hydroxymethylene*cyclo*hexanone and a little piperidine or diethylamine, condensation occurs with formation of 3-*cyano*-9-*hydroxyoctahydro*-2-*quinolone* (annexed formula I) and its dehydration product 3-*cyanohexahydro*-2-*quinolone* (formula II), the mixture being very difficult to separate. When condensation was


(I.)


(II.)

effected in solution in alcohol containing ammonia the sole product was the former substance, which was also obtained in the condensation of the amide of hydroxymethylene*cyclo*hexanone and ethyl cyanoacetate in absolute alcohol in the presence of an excess of diethylamine or piperidine. The substance is slowly converted by glacial acetic acid at 200—210° into the dehydration product (formula II), which was thus obtainable in prisms, m. p. 249° (decomp.). The latter was also produced in the condensation of the acetate of hydroxymethylene*cyclo*hexanone with cyanoacetamide in the presence of sodium ethoxide. The hydroxy-compound was methylated by sodium ethoxide and methyl iodide in alcoholic solution with formation of 3-*cyano*-9-*methoxyoctahydro*-2-*quinolone* (annexed formula, III), needles, m. p. 247°, which, on hydrolysis with sulphuric acid, yields an *acid*, m. p. 200—202°. Hydrolysis of the condensation products I and II yields a common product, *hexahydro*-2-*quinolone*-3-*carboxylic acid*, needles, m. p. 266—267°, at which temperature carbon dioxide is eliminated with formation of 2 : 3 : 5 : 6 : 8-*hexahydro*-2-*quinolone*, crystals, m. p. 202—204°; this substance can be distilled under reduced pressure without decomposition, and is converted by phosphorus pentachloride into oily 2-*chlorotetrahydroquinoline*. Quinoline could be obtained from the quinolone compound by successive distillations over heated zinc dust and heated lead oxide, the second distillation re-oxidising a small quantity of reduced quinoline derivatives formed in the first distillation.



(III.)

Condensation of 3-methylhydroxymethylene*cyclo*hexanone with cyanoacetamide likewise produced a mixture of an "aldol" compound and its dehydration derivative, the compounds obtained being respectively 3-*cyano*-9-*hydroxy*-7-*methyloctahydro*-2-*quinolone*, m. p. 272° (decomp.), and 3-*cyano*-7-*methylhexahydro*-2-*quinolone*, m. p. 256°. When hydrolysed with sulphuric acid these compounds were converted into 7-*methylhexahydro*-2-*quinolone*-3-*carboxylic acid*, needles, m. p. 259°, the decomposition of which on fusion yielded 7-*methylhexahydro*-2-*quinolone*, needles, m. p. 192—193°.

Ethyl cyanoacetate condenses with 3-methylhydroxymethylene*cyclo*hexanone in the presence of a little diethylamine, producing *ethy α-cyano-β-2-keto-4-methylcyclohexylidenepropionate*,

$$CHMe\begin{<}CH_2\cdot CO\\CH_2\cdot CH_2\end{>}C{:}CH\cdot CH(CN)\cdot CO_2Et,$$

crystals, m. p. 184—185°, which is converted by hydrolysis with concentrated sulphuric acid or alcoholic potassium hydroxide into the 7-methylhexahydro-2-quinolone-3-carboxylic acid just described; in alcoholic solution the ester reacts with hydrazine hydrate, yielding a *hydrazide*, m. p. 263—265° (decomp.).

4-*Methylhydroxymethylene*cyclo*hexanone*, b. p. 108—109°/25—27 mm., prepared in the usual manner, condenses with cyanoacetamide, forming 3-*cyano*-6-*methylhexahydro*-2-*quinolone*, m. p. 229°; by using alcoholic ammonia as the condensation agent, the intermediate "aldol" conden-

sation product could be obtained as a crystalline mass, m. p. above 290°. Hydrolysis of this product with sulphuric acid yielded 6-*methylhexahydro*-2-*quinolone*-3-*carboxylic acid*, m. p. 284°, fusion being attended by elimination of carbon dioxide and formation of 6-*methylhexahydro*-2-*quinolone*, m. p. 205—206°.

2-Methylhydroxymethylene*cyclo*hexanone, b. p. 112—114°/39 mm., undergoes condensation with cyanoacetamide, giving 3-*cyano*-8-*methylhexahydro*-2-*quinolone*, thin prisms, m. p. 242°; hydrolysis of this substance gave rise to 8-*methylhexahydro*-2-*quinolone*-3-*carboxylic acid*, m. p. 260—261°, the fusion of which was accompanied by formation of carbon dioxide and 8-*methylhexahydro*-2-*quinolone*, m. p. 142°.

Condensation of hydroxymethylenementhone with cyanoacetamide was effected as usual by piperidine or diethylamine, the product being 3-*cyano*-5-*methyl*-8-iso*propylhexahydro*-2-*quinolone*, thin prisms, m. p. 227—228° (decomp.); this substance was converted by hydrolysis into 5-*methyl*-8-iso*propylhexahydro*-2-*quinolone*-3-*carboxylic acid*, soft, colourless plates, m. p. 182—184°.

Diethylhydroxymethylene-ketone condenses readily with cyanoacetamide, forming 3-*cyano*-5-*methyl*-6-*ethyl*-2 : 3-*dihydro*-2-*pyridone*, $CEt\begin{matrix}<N---CO\\ CMe{\cdot}CH\end{matrix}>CH{\cdot}CN$, m. p. 230—231°; the corresponding 5-*methyl*-6-*ethyl*-2 : 3-*dihydro*-2-*pyridone*-3-*carboxylic acid*, melted at 287—288° with decomposition into carbon dioxide and 5-*methyl*-6-*ethyl*-2 : 3-*dihydro*-2-*pyridone*, prisms, m. p. 141°. The condensation product from ethyl ethoxymethyleneacetoacetate and ethyl cyanoacetate in the presence of ammonia was identical with that obtained by Errera (*loc. cit.*), who used sodium ethoxide as condensation agent; the resulting ethyl 3-cyano-α-picoline-5-carboxylate, however, was found to have m. p. 212—213°, instead of 208° as stated previously.

The instability of ethoxymethyleneacetylacetone rendered it necessary to effect the condensation with cyanoacetamide by adding the former compound to the sodium salt of the latter suspended in alcohol, when there was obtained the *sodium* salt of the condensation *product*, $C_9H_8O_2N_2$. This substance, m. p. 229—230°, forms a *methyl* ether, plates, m. p. 170°, and an *ethyl* ether, needles, m. p. 110°; on hydrolysis with concentrated hydrochloric acid it yields an acid, $C_9H_9O_4N$, m. p. 242—243°.

In a similar manner to the last, the condensation of dibenzylidene*cyclo*hexanone with sodiocyanoacetamide was effected, the product, $C_{23}H_{22}O_2N_2$, separating from acetic acid in prisms, m. p. 262—263°; on hydrolysis with hydrochloric acid, this substance formed a *substance*, $C_{22}H_{21}ON$, colourless needles, m. p. 248—249°, insoluble in aqueous acids and alkalis. This type of condensation with benzylidene derivatives of ketones is general. Styryl methyl ketone similarly gives as condensation product a *substance*, $C_{13}H_{14}O_2N_2$, m. p. 257—258°, insoluble in acids and alkalis. When the condensation was effected in alcoholic solution containing a little water in the presence of diethylamine, the resulting *product*, needles, m. p. 276°, had the composition $C_{13}H_{10}ON_2$, the mechanism of the change being uncertain; this substance yielded a *methyl* ether, $C_{14}H_{12}ON_2$, soft needles, m. p. 146°.

Acetyl*cyclo*hexanone condenses readily with cyanoacetamide with

formation of a substance, $C_{11}H_{12}ON_2$, needles, which begin to darken near 280°; this dissolves in alkali without decomposition, and on hydrolysis with hydrochloric acid is converted into a *substance*, $C_{10}H_{13}ON$, m. p. 235°. It is uncertain whether these compounds are derivatives of quinoline or of *iso*quinoline. D. F. T.

Spontaneous Oxidations in Presence of Aldehydes. MARIO BETTI and SERGIO BERLINGOZZI (*Gazzetta*, 1915, **45**, ii, 44—51).—The oxidation of *iso*-oxazolone derivatives in presence of benzaldehyde (this vol., i, 713) has been extended to 4-anisylidene- and 4-cinnamylidene-3-methyl*iso*oxazolones. In both cases, an *iso*oxazolecarboxylic derivative is obtained. In this oxidation it is assumed that the action of the alcoholic ammonia results in the opening of the *iso*oxazolonic anhydride ring with formation of the intermediate compound, $OH\cdot N{:}CR\cdot C(:CHPh)\cdot CO\cdot NH_2$, and that the hydrogen atoms of the OH and CH groups are then attacked by the atmospheric oxygen, this action being favoured by the presence of the aldehyde. It might, therefore, be expected that the oxime of benzylideneacetone and the stereoisomeric oximes of cinnamaldehyde, which are analogous to the above intermediate compound, would undergo similar oxidation, but in each of these cases the original oxime is recovered unchanged.

4-*Anisylidene-3-methyl*isooxazolone, $O<\begin{matrix}CO\cdot C{:}CH\cdot C_6H_4\cdot OMe\\ |\\ N{=}CMe\end{matrix}$, prepared by the interaction of ethyl acetoacetate, hydroxylamine, and anisaldehyde in aqueous alcohol, forms long, yellow, prismatic crystals, m. p. 174°. When heated with ammoniacal alcohol and benzaldehyde in a reflux apparatus, it yields the *amide* of 5-*methoxyphenyl*-3-*methyl*isooxazole-4-*carboxylic acid*,

$$O<\begin{matrix}C(C_6H_4\cdot OMe){:}C\cdot CO\cdot NH_2\\ |\\ N{=}CMe\end{matrix},$$

which forms shining, white needles, m. p. 195°; the corresponding *acid* forms long, flat needles, m. p. 178°.

Treatment of 4-benzylidene-3-methyl*iso*oxazolone with anisaldehyde in presence of alcoholic ammonia results in the separation of a small proportion of anishydramide and of 4-anisylidene-3-methyl*iso*oxazolone. When the latter is returned to the reacting mixture and this is heated with alcoholic ammonia, the amides of both 5-methoxyphenyl-3-methyl*iso*oxazole-4-carboxylic and 5-phenyl-3-methyl*iso*oxazole-4-carboxylic acids are obtained. Under these conditions, a condition of equilibrium evidently prevails, the methyl*iso*oxazole residue being combined partly with the benzaldehyde and partly with the anisaldehyde residue.

In presence of anisaldehyde, 4-anisylidene-3-methyl*iso*oxazolone is only very slowly oxidised, almost the whole of the oxazolone being recoverable unchanged after a considerable time.

5-*Styryl*-3-*methyl*isooxazole-4-*carboxylic acid*,

$$O<\begin{matrix}C(\cdot CH{:}CHPh){:}C\cdot CO_2H\\ |\\ N{=}CMe\end{matrix},$$

obtained as amide by treatment of 4-cinnamylidene-3-methyl*iso*oxazolone with alcoholic ammonia and benzaldehyde, forms a white, crystalline powder, m. p. 118—120°.

Attempts to oxidise benzylideneacetoneoxime by means of benzaldehyde or hydrogen peroxide or other peroxides were unsuccessful.

T. H. P.

Two Isomeric Diphenyl*iso*oxazolecarboxylic Acids. Mario Betti and Sergio Berlingozzi (*Gazzetta*, 1915, **45**, ii, 151—159).—3 : 5-Diphenyl*iso*oxazole-4-carboxylic acid, m. p. 233°, prepared from the corresponding amide by boiling with alkali (compare Betti, this vol., i, 896), was found to be accompanied by a small proportion of an isomeric acid, m. p. 153°. It is now found that the former acid is obtained in predominating proportion from the amide by the action of concentrated sodium hydroxide solution (50%) and the latter when the alkali is used in dilute solution (5%); intermediate concentrations give mixtures of the two acids. Both acids have normal molecular weights in boiling alcohol and both are strong acids able to decompose alkali carbonates. In both cases the sodium and potassium salts are readily soluble in water, giving neutral, lemon-yellow solutions, which become paler and deposit the salts on addition of alkali hydroxide. Their sulphur-yellow copper salts, which are insoluble in water, their garnet-red ferric salts, and salts of other metals, exhibit marked similarity Hydrolysis of the ethyl ester of the isomeride melting at 233° (*loc. cit.*) by either dilute or concentrated sodium hydroxide solution yields only the original acid, m. p. 233°. Since the molecule of the acid, m. p. 153°, contains a carboxyl and two phenyl groups, it must be regarded as 3 : 5-diphenyl*iso*oxazole-4-carboxylic acid and the nature of the isomerism remains to be explained.

The *acid*, m. p. 153°, forms pale yellow, prismatic needles; its *sodium* and *silver* salts were analysed.

T. H. P.

1 : 3-Oxazines (Pentoxazoles). S. Gabriel (*Annalen*, 1915, **409**, 305—327).—Corresponding with the conversion of acyl derivatives of α-amino-ketones into oxazoles under the influence of phosphorus pentachloride (Gabriel, A., 1910, i, 190, 431; Rüdenburg, A., 1914, i, 52; Bachstez, this vol., i, 306), it is now found that acyl derivatives of β-amino-ketones by similar treatment yield 1 : 3-oxazines:

$$R\cdot CO\cdot CH_2\cdot CH_2\cdot NH\cdot CO\cdot R_1 \rightarrow O\langle \begin{matrix} CR{:}CH \\ CR_1{=}N \end{matrix} \rangle CH_2.$$

These are much less stable than oxazoles; by simply warming their hydrochlorides the ring is broken, an unsaturated substance being formed which changes to the original acylated β-amino-ketone by migration of the acyl group from the oxygen to the nitrogen atom and subsequent ketonisation:

$$O\langle \begin{matrix} CR{:}CH \\ CR_1{=}N \end{matrix} \rangle CH_2 \xrightarrow{H_2O} R_1\cdot CO\cdot O\cdot CR{:}CH\cdot CH_2\cdot NH_2 \rightarrow$$

$$OH\cdot CR{:}CH\cdot CH_2\cdot NH\cdot CO\cdot R_1 \rightarrow R\cdot CO\cdot CH_2\cdot CH_2\cdot NH\cdot CO\cdot R_1.$$

ω-Benzoylaminopropiophenone, $NHBz\cdot CH_2\cdot CH_2\cdot COPh$, long prisms, m. p. 94·5—95·5°, prepared by benzoylating ω-aminopropiophenone in

the cold, is converted by warming with phosphorus pentachloride into the *hydrochloride*, needles, m. p. 177—178°, of 2:6-*diphenyl*-1:3-*oxazine*, $O<\begin{matrix}CPh=N\\CPh:CH\end{matrix}>CH_2$, colourless crystals, m. p. 86—87°, sintering at 84—85°. By warming with water, the hydrochloride is converted into the *hydrochloride*, $C_{16}H_{15}O_2N,HCl$, m. p. 184—184·5°, of the *O*-benzoate of the enolic form of ω-aminopropiophenone; the *dichromate*, $(C_{16}H_{15}O_2N)_2,H_2Cr_2O_7$, orange-yellow crystals, and *nitrate*, slender needles, m. p. 145—146° (decomp.), have been prepared. Attempts to isolate the base itself result in the formation of ω-benzoylaminopropiophenone, but its hydrochloride is converted into an *N-acetyl* derivative, OBz·CPh:CH·CH_2·NHAc, needles, m. p. 121°, by heating with acetic anhydride and sodium acetate at 100°, and reacts with saturated bromine water to form benzoic acid, the filtered solution then yielding with *N*/10-sodium picrate a *picrate*, yellow prisms, m. p. about 153° (decomp.), which is converted by hydrobromic acid into *α-bromo-β-aminopropiophenone hydrobromide*,

$$CHBrBz\cdot CH_2\cdot NH_2,HBr,$$

flattened needles or six-sided plates, m. p. 198° (decomp.).

Similar reactions can be effected with *ω-acetylaminopropiophenone*, leaflets, m. p. 76°. *6-Phenyl-2-methyl*-1:3-*oxazine hydrochloride*, $C_{11}H_{11}ON,HCl$, m. p. 171—172° (decomp.), forms needles or small prisms, and the *hydrochloride* of the *O*-acetate of enolic ω-aminopropiophenone, $C_{11}H_{13}O_2N,HCl$, crystallises in needles, m. p. 135—136°.

Methyl β-benzoylaminoethyl ketone, NHBz·CH_2·CH_2·COMe, needles, m. p. 81—82°, prepared by the benzoylation of methyl β-aminoethyl ketone hydrochloride, is converted by phosphorus pentachloride, without heating, into the *dichloride*, $CPhCl_2$·NH·CH_2·CH_2·COMe, needles, m. p. 135—136° (decomp.), by distillation at 180°/5 mm. into *2-phenyl-6-methyl*-1:3-*oxazine hydrochloride*, $C_{11}H_{11}ON,HCl$, needles, m. p. 148—149° (decomp.); the corresponding *platinichloride*,

$$(C_{11}H_{11}ON)_2,H_2PtCl_6,$$

forms yellow leaflets, and the *picrate*, stout needles, m. p. 175°, is converted by crystallisation from 50 % alcohol into the *picrate*,

$$C_{11}H_{13}O_2N,C_6H_3O_7N_3,$$

m. p. 155°, of the *O*-benzoate of the enolic form of methyl β-aminoethyl ketone.

Benzoyldiacetoneamine, NHBz·CMe_2·CH_2·COMe, needles, m. p. 101°, prepared by benzoylating diacetoneamine oxalate, reacts with phosphorus pentachloride on the water-bath to form, after treating the cold aqueous solution of the product with potassium hydrogen carbonate, *2-phenyl-4:4:6-trimethyl*-1:3-*oxazine*, which has a biting taste and an odour of bergamot oil, and decomposes by distillation into benzonitrile and, probably, mesityl oxide. The *hydrochloride*, $C_{13}H_{15}ON,HCl$, rhombohedra or short prisms, m. p. 174°, and *platinichloride*, orange-yellow needles, decomp. 195°, are described; the former is easily converted by hot water into the *hydrochloride*, $C_{13}H_{17}O_2N,HCl$, needles, m. p. 169°, of the *O*-benzoate of enolic diacetoneamine, and reacts with bromine water to form benzoic acid and β-bromodiacetoneamine, isolated as the *picrate*, CHBrAc·CMe_2·NH_2,$C_6H_3O_7N_3$, needles, m. p. 151°.

Acetyldiacetoneamine, b. p. about 237—245° (not pure), is converted in a similar manner to the benzoyl derivative into 2 : 4 : 4 : 6-*tetramethyl*-1 : 3-*oxazine*, b. p. 144°, which forms a *picrate*, plates and prisms, m. p. 159°, and is decidedly less stable than the phenyltrimethyl-1 : 3-oxazine.

By heating with potassium acetate and acetic anhydride, *o*-hydroxybenzylamine hydriodide is converted into *diacetyl-o-hydroxybenzylamine*, $OAc\cdot C_6H_4\cdot CH_2\cdot NHAc$, flat needles, m. p. 107°. The *monoacetyl* derivative, m. p. 140°, is prepared by boiling the diacetyl derivative with hydrochloric acid, by treating an aqueous solution of the preceding hydriodide and potassium hydrogen carbonate with acetic anhydride at 0°, or by the action of nitrous acid on acet-*o*-aminobenzylamide. It is converted by hydrogen chloride, or, better, by phosphorus pentasulphide at about 140° into 2-*methyl*-1 : 3-*benzoxazine*, $C_6H_4<\begin{matrix}O-\!\!-C\,Me\\ \|\quad\ \|\\ CH_2\cdot N\end{matrix}$, an oil which has an odour of quinoline and a biting taste, and is very readily converted into *N*-acetyl-*o*-hydroxybenzylamine by water; the *aurichloride*, $C_9H_9ON,HAuCl_4$, golden-yellow needles, m. p. 134—135°, *platinichloride*, brownish-yellow needles, m. p. about 207—209° (decomp.), and *picrate*, leaflets, m. p. about 187° (decomp.), have been prepared. Methyl-1 : 3-benzoxazine can also be prepared by heating diacetyl-*o*-hydroxybenzylamine in hydrogen chloride at 140—160°.

The migration of an acyl group from oxygen to nitrogen is also exhibited by the β-aminoethyl, β-aminopropyl, and γ-aminopropyl esters of benzoic acid; by warming with water these are converted into benz-β-hydroxyethylamide, benz-β-hydroxypropylamide, and *benz-γ-hydroxypropylamide*, $NHBz\cdot[CH_2]_3\cdot OH$, needles, m. p. 60—60·5° respectively. C. S.

Hydantoins. XXXIII. Condensation of Cinnamaldehyde with Hydantoins. Treat B. Johnson and Richard Wrenshall (*J. Amer. Chem. Soc.*, 1915, **37**, 2133—2144).—It has been shown by Wheeler and Brautlecht (A., 1911, i, 501) that cinnamaldehyde condenses with 2-thio-1-phenylhydantoin with formation of 2-thio-1-phenyl-4-cinnamylidenehydantoin, and it has now been found that hydantoin and 2-thiohydantoin also undergo condensation with this aldehyde.

4-Cinnamylidenehydantoin, $CHPh:CH\cdot CH:C<\begin{matrix}CO-\!\!-NH\\ \|\quad\ \|\\ NH\cdot CO\end{matrix}$, m. p. 272—273° (decomp.), crystallises in yellow prisms, and on reduction with sodium amalgam is converted into *γ-phenylpropenylhydantoic acid*, $NH_2\cdot CO\cdot NH\cdot CH(CH:CH\cdot CH_2Ph)\cdot CO_2H$, m. p. between 142° and 161° (decomp.), which forms colourless, diamond-shaped plates. When this acid is digested with barium hydroxide, *α-amino-δ-phenyl-Δ$^{\beta}$-pentenoic acid*, $CH_2Ph\cdot CH:CH\cdot CH(NH_2)\cdot CO_2H$, m. p. 247—248° (decomp.), is obtained, which forms long, colourless needles. By the action of hydrochloric acid on γ-phenylpropenylhydantoic acid, *4-γ-phenylpropenylhydantoin*, $CH_2Ph\cdot CH:CH\cdot CH<\begin{matrix}CO-\!\!-NH\\ \|\quad\ \|\\ NH\cdot CO\end{matrix}$, m. p. 160—161°, is produced, which crystallises in long needles. If α-amino-δ-phenyl-Δ$^{\beta}$-

pentenoic acid is warmed with ammonium thiocyanate and acetic anhydride, *2-thio-3-acetyl-4-γ-phenylpropenylhydantoin*,

$$CH_2Ph\cdot CH{:}CH\cdot CH{<}\begin{matrix}CO-NH\\ |\\ NAc\cdot CS\end{matrix},$$

m. p. 97—98°, is obtained, which forms orange plates. When this compound is heated with hydrochloric acid, it is converted into *2-thio-4-γ-phenylpropenylhydantoin*, $CH_2Ph\cdot CH{:}CH\cdot CH{<}\begin{matrix}CO-NH\\ |\\ NH\cdot CS\end{matrix}$, m. p. 126—127°, which crystallises in needles or distorted prisms, and on desulphurisation with chloroacetic acid yields 4-γ-phenylpropenylhydantoin.

2-Thio-4-cinnamylidenehydantoin, $CHPh{:}CH\cdot CH{:}C{<}\begin{matrix}CO-NH\\ |\\ NH\cdot CS\end{matrix}$, m. p. 262—263°, forms red, prismatic columns; a yellow modification of this compound was also obtained containing 1 mol. of acetic acid of crystallisation. On reducing this compound with sodium amalgam, *thio-γ-phenylpropenylhydantoic acid*,

$$NH_2\cdot CS\cdot NH\cdot CH(CH{:}CH\cdot CH_2Ph)\cdot CO_2H,$$

is obtained as an oil which is converted by hydrochloric acid into 2-thio-4-γ-phenylpropenylhydantoin. By the partial reduction of 2-thio-4-cinnamylidenehydantoin with zinc dust and glacial acetic acid, a compound, probably *2-thio-4-γ-phenylallylhydantoin*, is obtained as a powder without a definite m. p. When 2-thio-4-cinnamylidenehydantoin is heated in a sealed tube with chloroacetic acid, it is converted into 4-cinnamylidenehydantoin.

4-α-Bromocinnamylidenehydantoin, $CHPh{:}CH\cdot CBr{:}C{<}\begin{matrix}CO-NH\\ |\\ NH\cdot CO\end{matrix}$, m. p. 290—295° (decomp.), obtained by the action of bromine on 4-cinnamylidenehydantoin, forms yellow needles. *4-β-Bromocinnamylidenehydantoin*, $CHPh{:}CBr\cdot CH{:}C{<}\begin{matrix}CO-NH\\ |\\ NH\cdot CO\end{matrix}$, m. p. 226—227° (decomp.), prepared by condensing bromocinnamaldehyde with hydantoin, crystallises in yellow prisms. *3-Acetyl-4-cinnamylidenehydantoin*, $CHPh{:}CH\cdot CH{:}C{<}\begin{matrix}CO-NH\\ |\\ NAc\cdot CO\end{matrix}$, m. p. 241—242°, forms yellow prisms and is readily hydrolysed by hydrochloric acid with formation of cinnamylidenehydantoin. E. G.

Hydantoins. XXXIV. Interaction of Hippuric Acid with Thiocyanates. TREAT B. JOHNSON, ARTHUR J. HILL, and BERNARD H. BAILEY (*J. Amer. Chem. Soc.*, 1915, **37**, 2406—2416).—Johnson and Nicolet (A., 1912, i, 53; 1913, i, 399) and Johnson (A., 1913, i, 203) have shown that ammonium or potassium thiocyanate reacts with hippuric acid in presence of acetic anhydride with formation of 2-thio-3-benzoylhydantoin, but that when the potassium salt is used the yield is only about 50% of that obtained when the ammonium salt is employed. The present work was undertaken with the object of discovering the cause of this difference in the behaviour of the two salts.

It is shown that the view that ammonium thiocyanate, when heated with acetic anhydride undergoes a rearrangement into thiocarbamide, which then reacts with the hippuric acid, is untenable. Nencki and Leppert (this Journal, 1873, 1224) and Klason (A., 1889, 227) have shown that, under certain conditions, ammonium thiocyanate and acetic anhydride react, with formation of acetylperthiocyanic acid. This substance does not react with hippuric acid in acetic anhydride solution to form 2-thio-3-benzoylhydantoin. When dry ammonium thiocyanate is heated with acetic anhydride at 100°, *iso*dithiocyanic acid is produced, but neither mono- nor di-acetylthiocarbamide is formed. These results support the assumption that thiocyanic acid is first formed when acetic anhydride and acetic acid react with ammonium thiocyanate.

Brunner (this vol., i, 224) has shown that potassium cyanate reacts with certain anhydrides with formation of secondary amides, and it therefore seemed of interest to determine whether other anhydrides than acetic anhydride could be employed to effect a thiohydantoin condensation with hippuric acid. With propionic anhydride, 2-thio-3-benzoylhydantoin is produced just as smoothly as with acetic anhydride, and no propionylthiocarbamide is formed. With benzoic anhydride, however, only a small yield of the thiohydantoin is obtained, but at least 50% of the ammonium thiocyanate is converted into benzoylthiocarbamide. In the absence of hippuric acid, ammonium thiocyanate and benzoic anhydride react at 100° with formation of the same benzoylthiocarbamide. In this case, therefore, the ammonium thiocyanate undergoes rearrangement into thiocarbamide, which is then converted into the benzoyl derivative; the benzoic anhydride thus acts catalytically.

When potassium cyanate is heated with hippuric acid in presence of acetic anhydride and glacial acetic acid, cyanuric acid is produced. The same result is obtained if aceturic acid or glycine is used instead of hippuric acid.

The behaviour of the thiocyanates of ammonium, lithium, sodium, potassium, magnesium, calcium, strontium, barium, manganese, and zinc towards hippuric acid in acetic anhydride solution has been investigated, and it has been found that all these salts, except zinc thiocyanate, interacted to form the 2-thio-3-benzoylhydantoin, but that they furnished very different yields. Ammonium thiocyanate gave a 93·4% yield, the magnesium salt a 77% yield, whereas none of the other salts gave a yield of more than 48%.

When thiocarbamide is heated with hippuric acid in presence of acetic anhydride and acetic acid, 2-thio-3-benzoylhydantoin is not produced, but acetylthiocarbamide is formed. E. G.

Attempts to Obtain Amino-derivatives of Barbituric Acids. G. Fiore (*Boll. chim. farm.*, 1915, **54**, 449—451).—Attempts have been made to prepare amino-derivatives of barbituric acids, especially those of veronal of the type $CEt_2<\begin{matrix}CO\cdot N(NH_2)\\CO\text{——}NH\end{matrix}>CO$, by the action of diethylmalonyl chloride on semicarbazones. From diethylmalonyl chloride and benzylidenesemicarbazone, Freund and Fleischer (A., 1911, i, 236) obtained 3 : 5-diketo-1 : 2-diethylmalonyl-

4 : 4-diethylpyrazolidine. The author finds, however, that when dissolved in pyridine, which was added to fix the hydrogen chloride liberated during the reaction, diethylmalonyl chloride and acetonesemicarbazone yield diethylmalonylhydrazide (compare Einhorn, A., 1908, i, 316); the latter is also obtained, together with hydrazodicarbonamide, when the reaction is carried out in aqueous alkali solution. No better result is obtained from acetonethiosemicarbazone and diethylmalonyl chloride, which yield diethylmalonylhydrazide, in addition to resinous products. With diethylmalonyl chloride and nitrocarbamide, complete decomposition into gaseous products takes place, and when veronal is heated with hydrazine in a closed tube, the ureide residue is entirely displaced by the hydrazine residue with formation of diethylmalonylhydrazide. T. H. P.

Pyrimidines. LXXV. Pyrimidine Aldehydes and their Biochemical Interest (Thiouracilaldehyde). Treat B. Johnson and Leonard H. Cretcher, jun. (*J. Amer. Chem. Soc.*, 1915, **37**, 2144—2151).—The work described in this paper was undertaken with the object of preparing cyclic aldehydes of the pyrimidine series. Such compounds have not been described hitherto and would probably be of value for the synthesis of pyrimidine compounds of considerable biochemical interest.

When ethyl γ-diethoxyacetoacetate (Dakin and Dudley, T., 1914, **105**, 2455) is heated with thiocarbamide and sodium ethoxide, the *diethylacetal* of *2-thio-4-uracilaldehyde*, $NH<^{CS\cdot NH}_{CO\cdot CH}>C\cdot CH(OEt)_2$, m. p. 160°, is produced which crystallises in thick, rhombic blocks; it could not be desulphurised by mercuric oxide, lead hydroxide, or chloroacetic acid. On hydrolysis with hydrochloric acid, the acetal is converted quantitatively into *2-thiouracilaldehyde*,

$$NH<^{CS\cdot NH}_{CO\cdot CH}>C\cdot CHO,H_2O,$$

which forms golden-yellow, glistening plates; it darkens at about 230° and decomposes at 250°. The aldehyde reduces ammoniacal silver nitrate and Fehling's solution. Its *phenylhydrazone* crystallises in yellow needles and does not melt below 300°.

By the action of ethyl bromide and sodium ethoxide on the diethylacetal of 2-thio-4-uracilaldehyde, the *diethylacetal* of *2-ethylthiol-4-aldehydodihydro-6-pyrimidone*, $NH<^{C(SEt):N}_{CO---CH}>C\cdot CH(OEt)_2$, m. p. 128°, is obtained, which forms colourless, slender needles, and when boiled with hydrochloric acid yields *uracil-4-aldehyde*,

$$NH<^{CO\cdot NH}_{CO\cdot CH}>C\cdot CHO,H_2O,$$

which crystallises in rosettes of small prisms and does not melt below 300°. *2-Ethylthiol-4-aldehydodihydro-6-pyrimidone*, m. p. 145°, obtained by carefully hydrolysing the acetal with dilute hydrochloric acid, forms long prisms.

The *diethylacetal* of *2-methylthiol-4-aldehydodihydro-6-pyrimidone*, $NH<^{C(SMe):N}_{CO---CH}>C\cdot CH(OEt)_2$, m. p. 133°, crystallises in needles. E. G.

Pyrimidines. LXXVI. New Methods of Synthesising 2-Keto pyrimidines and their Sulphur Analogues. TREAT B. JOHNSON and A. WILLARD JOYCE (*J. Amer. Chem. Soc.*, 1915, **37**, 2151—2164).—Although considerable attention has been given to the pyrimid-2 : 6-diones, of which uracil is the type, the pyrimidones and the simple pyrimidine compounds have hitherto been little studied, and the present work was therefore undertaken.

6-Chloro-5-ethoxy-2-ethylthiolpyrimidine (Johnson and McCollum, A., 1906, i, 704) cannot be desulphurised by heating with chloroacetic acid. When boiled with dilute alcohol and zinc dust, it is converted into *5-ethoxy-2-ethylthiolpyrimidine*, $N\leqslant\begin{matrix}C(SEt)\text{—}N\\CH{:}C(OEt)\end{matrix}\geqslant CH$, m. p. 31—32°, which forms thin, transparent plates, or prisms; another *compound*, m. p. 126—127°, is also produced which crystallises in needles. *5-Ethoxy-2-ethylthiolpyrimidine hydrochloride* has m. p. 120—121°, and the *platinichloride*, m. p. 165—166°. Attempts were made to desulphurise 5-ethoxy-2-ethylthiolpyrimidine but without success.

2 : 6-Dichloro-5-ethoxypyrimidine has m. p. 51°, and not 41—42° as recorded by Johnson and Guest (A., 1909, i, 745). When reduced with zinc dust, it furnishes *2-chloro-5-ethoxypyrimidine*, $N\leqslant\begin{matrix}CCl\text{——}N\\CH{:}C(OEt)\end{matrix}\geqslant CH$, m. p. 70°, which forms thin, transparent plates, and is converted by potassium hydrogen sulphide into *2-thio-5-ethoxydihydropyrimidine*, $NH\leqslant\begin{matrix}CS\text{——}N\\CH{:}C(OEt)\end{matrix}\geqslant CH$, m. p. 192—193°, which crystallises in pale yellow columns; the latter compound is accompanied by a small quantity of the *disulphide*, $\left(OEt\cdot C\leqslant\begin{matrix}CH{:}N\\CH\cdot N\end{matrix}\geqslant C\right)_2S_2$, m. p. 125°. When 2-thio-5-ethoxydihydropyrimidine is heated with ethyl bromide in presence of potassium hydroxide, it is converted into 5-ethoxy-2-ethylthiolpyrimidine, and when boiled with chloroacetic acid, it yields *5-ethoxypyrimidine-2-thiolacetic acid*, $CO_2H\cdot CH_2\cdot S\cdot C\leqslant\begin{matrix}N{:}CH\\N\cdot CH\end{matrix}\geqslant C\cdot OEt$, m. p. 137—138°, which crystallises in needles.

2 : 5-*Diethoxypyrimidine*, $N\leqslant\begin{matrix}C(OEt)\text{—}N\\CH{:}C(OEt)\end{matrix}\geqslant CH$, b. p. 142°/24 mm., m. p. 19°, obtained by the action of sodium ethoxide on 2-chloro-5-ethoxypyrimidine, forms large, transparent plates; its *hydrochloride* crystallises in colourless needles, and the *platinichloride* has m. p. 176° (decomp.).

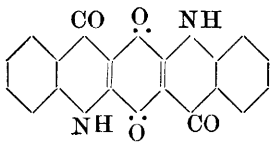
When 6-chloro-2-ethylthiolpyrimidine (Wheeler and Johnson, A., 1903, i, 526) is heated with zinc dust and dilute alcohol, *2-ethylthiolpyrimidine*, $N\leqslant\begin{matrix}C(SEt)\cdot N\\CH\text{=}CH\end{matrix}\geqslant CH$, b. p. 115°/20 mm., is obtained as a colourless oil with a pungent odour; its *hydrochloride* has m. p. 98—99°, and its *platinichloride* m. p. 166°. By the action of concentrated hydrochloric acid on 2-ethylthiolpyrimidine, *dihydropyrimid-2-one*, $NH\leqslant\begin{matrix}CO\text{—}N\\CH{:}CH\end{matrix}\geqslant CH$, a pale yellow, amorphous substance, is produced, which does not melt below 320°; its *hydrochloride* has m. p. 203—205°.

2-*Ethylthiol*-4-*methylpyrimidine*, $N\leqslant\begin{matrix}C(SEt)\cdot N\\ CMe:CH\end{matrix}\geqslant CH$, b. p. 123—124°/18—19 mm., is obtained as an oil by reducing 6-chloro-2-ethylthiol-4-methylpyrimidine (Johns, A., 1908, i, 917) with zinc dust; its *hydrochloride* has m. p. 141—142°, and its *platinichloride*, m. p. 165—166°. E. G.

Oxidation of Phenolic Substances. Adolf Jolles (*J. pr. Chem.*, 1915, [ii], **92**, 202—207).—Other phenolic substances, besides thymol, lead to the formation of indigoid and indolignoid compounds (Friedländer, A., 1908, i, 673) when oxidised simultaneously with indoxyl (compare this vol., i, 838). As a source of indoxyl, technical indoxylic acid may be used, or better, *N*-acetylindoxyl, which can be obtained purer. When a mixture of the latter with thymol is dissolved in glacial acetic acid and then mixed with a solution of ferric chloride in concentrated hydrochloric acid, 4-cymol-2-indolindolignone is formed, whilst α-naphthol gives a mixture of "2-naphthol-2-indolindigo" and 4-naphthol-2-indolindolignone (Bezdzik and Friedländer, *loc. cit.*) J. C. W.

The Biochemistry of the Action of Rays. IV. Photochemical Formation of Indigotin from Indican. Carl Neuberg and Erwin Schwenk (*Biochem. Zeitsch.*, 1915, **71**, 219—225).—In the presence of various catalysts (ferrous sulphate, uranyl sulphate, manganous sulphate, cerous sulphate, sodium anthraquinone-2:7-disulphonate, etc.), indican is converted into indigotin by the action of ultra-violet rays. S. B. S.

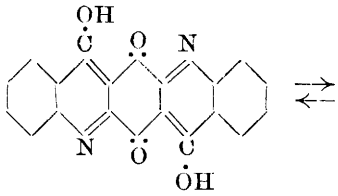
Quinonediacridone. V. V. Scharvin (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1260—1268).—*Quinonediacridone* (annexed formula), which is the anhydride of quinonedianthranilic acid (quinonebis-*o*-aminobenzoic acid) (compare Ville and Astre, A., 1895, i, 466, 533; Astre and Stévignon, A., 1897, i, 525) and is prepared by heating the latter with concentrated sulphuric acid at 200°, forms slender, orange needles, and is characterised by sparing solubility in all the ordinary solvents and by very slight reactivity. It contains the indigoid grouping, $C_6H_4\leqslant\begin{matrix}CO\\ NH\end{matrix}\geqslant$, and, like indigotin, exhibits feeble basic properties; its *sulphate*,



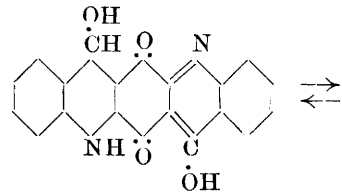
$$C_{20}H_{10}O_4N_2,H_2SO_4,$$

was prepared. Its-*dibromo*-derivative, $C_{20}H_8O_4N_2Br_2$, which forms a red powder, and its *dinitro*-derivative, $C_{20}H_8O_8N_4$, which is more markedly red than the parent compound, also show slight solubility. Sulphonation with fuming sulphuric acid containing 50% of the anhydride yields a product which is readily soluble in water but forms a sparingly soluble sodium salt. Quinonediacridone also exhibits acid characters and forms with potassium hydroxide an insoluble red salt, which is readily hydrolysed by water. This behaviour indicates that its structure is probably represented, not by the formula given above,

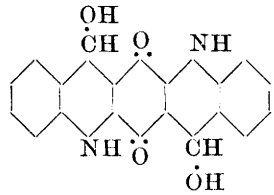
which is deduced from the method of preparation, but by formula I. (*vide infra*). The latter also explains the behaviour of quinonediacridone on reduction by means of hyposulphite, this yielding first a green compound (II) and then a bluish-violet compound (III) :



Orange (I)



Green (II).



Bluish-violet (III).

Compound (III), $C_{20}H_{14}O_4N_2$, forms microscopic, rectangular plates, and is somewhat more readily soluble than quinonediacridone. In concentrated sulphuric acid it dissolves, giving a pure blue solution, which soon becomes green and then yellow, dilution of the final liquid resulting in the precipitation of quinonediacridone; gentle heating accelerates these changes.

Quinonediacridone and its derivatives behave as colouring matters. Quinonediacridone itself colours wool and silk yellow in an acid bath. Cotton is dyed only with the help of reduced quinonediacridone; the tissue, coated with a liquid paste of quinonediacridone and gum and then dried, assumes a green colour when immersed in alkaline hyposulphite solution, and a stable red colour after subsequent oxidation in the air. If the reduction proceeds as far as the development of the violet colour, oxidation is considerably retarded. Albuminous fibres are, however, best dyed by means of the sulphoderivative of quinonediacridone in a faintly acid bath, silk then assuming a splendid, golden colour; if, in addition, hyposulphite is present, albuminous fibres are dyed blue. In view of the insolubility of quinonediacridone and particularly of its stability towards different reagents, these dyes are characterised by great fastness, which is also exhibited towards the action of light. When exposed in an atmosphere of hydrogen to the light, the colouring matters readily undergo reduction, this action being especially marked with the sulpho-acid.

T. H. P.

Pyrazo-oxazines and Oxazo-oxazines. Two New Types of Bisheterocyclic Derivatives with Naphthalenoid Linking. Mario Betti (*Gazzetta*, 1915, **45**, ii, 75—81).—The interaction of

1-phenyl-3-methyl-5-pyrazolone (1 mol.), benzaldehyde (2 mols.), and β-naphthylamine (1 mol.) in alcoholic solution yields: (1) 4-benzylidene-bis-1-phenyl-3-methyl-5-pyrazolone (compare Lachowicz, A., 1897, i, 119) and (2) the *pyrazo-oxazine* derivative, $N\!\leqslant\!\begin{matrix}CMe\cdot C\cdot CHPh\cdot N\cdot C_{10}H_7\\ \|\quad\quad\quad\quad\quad\quad\\ NPh\cdot C.O\!-\!-\!-\!-\!-CHPh\end{matrix}$, which forms tufts of large, white, acicular crystals, m. p. 227°, and remains unchanged when boiled with either 20% hydrochloric acid or 50% sodium hydroxide solution. The naphtha*iso*oxazine derivatives corresponding with compound (2) are formed by way of an intermediate additive compound of the general type, $C_8H_6\!<\!\begin{matrix}C\cdot CHR\cdot NHR\\ \|\\ C\cdot OH\end{matrix}$ (A., 1901, i, 753), and in the present case, when the reaction proceeds in benzene, a similar additive compound appears to be formed, but attempts to purify it result in its decomposition.

The interaction of 4-benzylidene-3-methyl*iso*oxazolone (1 mol.) (compare Schiff and Betti, A., 1897, i, 493), benzaldehyde (1 mol.), and β-naphthylamine (1 mol.) yields the *oxazo-oxazine* derivative, $N\!\leqslant\!\begin{matrix}CMe\cdot C\cdot CHPh\cdot N\cdot C_{10}H_7\\ O\!-\!-\!-\!C\cdot O\!-\!-\!-\!-CHPh\end{matrix}$, which forms tufts of slender, silky needles, m. p. 257° (decomp.), and withstands the action of boiling 10% hydrochloric acid or 20% sodium hydroxide solution. T. H. P.

Hydantoins. XXXV. New Method of Synthesising Glycocyamidine Compounds and the Conversion of Glycocyamidine into Isomerides of Creatinine. Treat B. Johnson and Ben H. Nicolet (*J. Amer. Chem. Soc.*, 1915, **37**, 2416—2426).—An account is given of a new and easy method of preparing glycocyamidine and its alkyl derivatives by the action of amines on ethyl benzoyl-ψ-ethylthiohydantoate.

When a solution of ethyl benzoyl-ψ-ethylthiohydantoate (Wheeler, Nicolet, and Johnson, A., 1911, i, 1031) in alcohol is treated with aqueous ammonia, ethyl mercaptan is evolved, and 2-*benzoylglycocyamidine*, $NBz{:}C\!<\!\begin{matrix}NH\cdot CO\\ |\\ NH\cdot CH_2\end{matrix}$, is produced, which forms colourless needles; it has no definite m. p., but decomposes at 230°.

By the action of methylamine on ethyl benzoyl-ψ-ethylthiohydantoate, 2-*benzoyl*-1-*methylglycocyamidine*, $NBz{:}C\!<\!\begin{matrix}NMe\cdot CO\\ |\\ NH\!-\!CH_2\end{matrix}$, m. p. 214°, distorted needles, is produced together with a small quantity of 1-benzoyl-2-methylglycocyamidine; the latter compound was not isolated. When 2-benzoyl-1-methylglycocyamidine (benzoyl*iso*creatinine) is heated with strong hydrochloric acid, 1-methylglycocyamidine hydrochloride is produced, identical with the compound described by Korndörfer (A., 1905, i, 30); the picrate has m.p. 196°, and the aurichloride m. p. 166° (decomp.). By the condensation of benzaldehyde with the crude hydrochloride obtained by the hydrolysis of the mixture of 2-benzoyl-1-methyl- and 1-benzoyl-2-methyl-glycocyamidine, 4-*benzylidene*-1-*methylglycocyamidine*, $NH{:}C\!<\!\begin{matrix}NMe\cdot CO\\ |\\ NH\!-\!C{:}CHPh\end{matrix}$, m. p. 246—247° (decomp.),

flat, orange-coloured prisms, is produced together with a small quantity of 4-*benzylidene-2-methylglycocyamidine*, $NMe{:}C\begin{cases}NH\cdot CO\\ |\\ NH\cdot C{:}CHPh\end{cases}$, needle-like prisms, m. p. 223°. Associated with the 4-benzylidene-1-methylglycocyamidine was a small amount of a *substance*, m. p. 237—239°, which was probably a stereoisomeric modification. 4-Benzylidene-2-methylglycocyamidine was also obtained by heating 2-ethylthiol-4-benzylidene-1 : 5-dihydro-5-glyoxalone (Johnson and Nicolet, A., 1912, i, 808) with methylamine, and from 2-thiohydantoin by the following procedure. 2-Thiohydantoin was converted into 2-methylthiolhydantoin (Komatsu, A., 1911, i, 684) by alkylation with methyl iodide, and this compound into 2-*methylglycocyamidine* by heating it with methylamine. The latter compound was not isolated, but on condensation with benzaldehyde it yielded 4-benzylidene-2-methylglycocyamidine.

4-Benzylideneglycocyamidine (Ruhemann and Stapleton, T., 1900, **77**, 247), m. p. 297°, can be obtained by the condensation of glycocyamidine with benzaldehyde; it reacts with methyl iodide in presence of potassium hydroxide to form 4-benzylidene-1-methylglycocyamidine.

Experiments are described which show that under certain conditions 2-methylglycocyamidine undergoes molecular rearrangement into 1-methylglycocyamidine, and render it evident that in the alkylation of glycocyamidines in presence of alkali, different alkyl derivatives can be formed according to the conditions employed. E. G.

A New Method of Preparation of Triazoles. KARL BRUNNER (*Monatsh.*, 1915, **36**, 509—534. Compare this vol., i, 225).—It has already been shown that diacetamide reacts with semicarbazide hydrochloride in aqueous solution at the ordinary temperature with formation of hydrazoformamide and dimethyltriazole. The reaction is now being extended to other secondary amides and it is found that di-*n*-butyramide in this way gives dipropyltriazole in good yield; dibenzamide reacts with semicarbazide hydrochloride in the fused condition at 150—160°, giving diphenyltriazole, but the result in aqueous solution is poor; sodium diformamide gives only a trace of triazole whether the reaction occurs in the fused or the dissolved state.

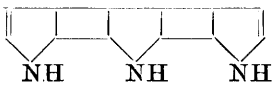
In the case of diacetamide, which was more thoroughly investigated, the semicarbazide must be present as the hydrochloride or acetate, because with the free base no dimethyltriazole is produced. Attempts to obtain dimethyltriazole by the action of hydrazine or its salts in place of semicarbazide were fruitless.

The method of interaction between secondary amides and semicarbazide hydrochloride is believed to be of a type quite distinct from previous syntheses of triazole compounds, and to be somewhat analogous to the interaction of β-diketones with the same reagent, a dimethyltriazolecarboxylamide, $\begin{matrix}N{:}CMe\\ |\\ CMe{:}N\end{matrix}\!\!>\!N\cdot CO\cdot NH_2$, being assumed as a primary condensation product, which reacts with a second molecule of semicarbazide, yielding dimethyltriazole and hydrazoformamide. This resemblance to the β-diketones is confirmed by the discovery that

diacetamide reacts with phenylhydrazine acetate in hot aqueous solution, giving 1-phenyl-3 : 5-dimethyl-1 : 2 : 4-triazole. The following compounds of dimethyltriazole are described :—hydrochloride, m. p. 199—200° ; nitrate, m. p. 126—127° (corr.), decomp. at 130° ; *additive compound*, $C_4H_7N_3,AgNO_3$, leaflets, m. p. 222—223° (corr.) ; *mercurichloride*, $C_4H_7N_3,4HgCl_2$, microscopic grains, m. p. 185°. For the preparation of the last substance, dimethyltriazole hydrochloride is taken with an excess of mercuric chloride ; if this salt is taken with a solution of the free base, the product is *mercurydimethylpyrazole mercurichloride*, $(C_4H_6N_3)_2Hg,2HgCl_2$, a crystalline, sandy powder, m. p. 242—243°.

1-Phenyl-3 : 5-dimethyl-1 : 2 : 4-triazole (compare Pellizzari, A., 1911, i, 1036) forms a hydrochloride, m. p. 219—220°, a *mercurichloride*, $C_{10}H_{11}N_3,HgCl_2$, needles, m. p. 187—188°, and a crystalline *aurichloride*. D. F. T.

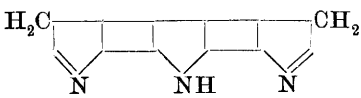
Nature and Structure of Tripyrrole. V. V. Tschelincev, B. V. Tronov, and B. I. Voskresenski (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1224—1244).—On the basis of the conversion of tripyrrole into indole, with removal of 1 mol. of ammonia and 1 mol. of pyrrole, Dennstedt and Voigtländer (A., 1894, i, 259) ascribed to this compound the annexed structure, which is supported by the formation from 2- and 3-monosubstituted and 2 : 3-disubstituted pyrroles of binary type (A., 1887, 598; 1888, 849; 1889, 400), these giving substituted derivatives of indole when heated with sulphuric acid. The results obtained by the authors show that tripyrrole has not the configuration given above and that the properties differ somewhat from those described by Dennstedt. Condensation experiments have also been carried out with 1-substituted derivatives of pyrrole.



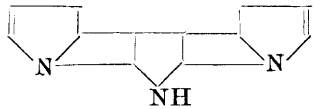
Tripyrrole hydrochloride, $C_{12}H_{15}N_3,HCl$, is best obtained by passing dry hydrogen chloride through a benzene solution of pyrrole. Tripyrrole itself is a crystalline product melting at 86—90° to a transparent liquid and beginning to decompose at 130°. The absence of sharpness in the melting point is ascribed to the readiness with which this compound undergoes change and since the percentage of nitrogen present, instead of 20·89, is found to be 19·64 and, after a few days, 19·11, and similar diminutions occur in the carbon and hydrogen contents, it is assumed that oxidation takes place ; Dennstedt (*loc. cit.*) gave no analytical results. The latter author describes the transformation of tripyrrole, when kept, into a product, m. p. 121°, of unchanged composition. This product is now found to melt at 124—130°, and to be the result, not only of oxidation, but also of condensation, the molecular weight in freezing bromoform or benzene gradually increasing from 264 for the freshly prepared tripyrrole to 368 after a month.

According to Dennstedt's formula, tripyrrole should react with magnesium ethyl bromide or magnesium propyl iodide, giving a derivative containing three MgBr residues, and this should be converted into a triacetyl derivative of tripyrrole by treatment with ethyl

acetate. Hess and Wissing's results (A., 1914, i, 725) indicate the possibility of reaction, with the magnesium alkyl haloid, not only of the 1-hydrogen atoms, but also of the 2-hydrogen atoms of the outer pyrrole nuclei at least. Experiment shows, however, that treatment with magnesium propyl iodide gives, per gram-mol. of pyrrole or 2-acetylpyrrole, 1 gram-mol. of propane, whilst with 1-methylpyrrole, no gas is liberated in 6—8 minutes and only 0·3 gram-mol. in 30 minutes. Similar experiments with tripyrrole (1 gram-mol.) gave 1·31 and 1·29 gram-mols. of propane, and with tripyrrole hydrochloride, 1·24 gram-mols. From these results it is evident that the molecule of tripyrrole contains only one imino-hydrogen atom and that Dennstedt's formula, containing three imino-hydrogen atoms, is incorrect. It may be that the compound has the tautomeric formula (I), but in this case the action of the magnesium propyl iodide should convert it into the form containing three imino-groups and should therefore result in the liberation of three molecules, and not one molecule only, of propane. It seems more probable that tripyrrole possesses the configuration II or III.

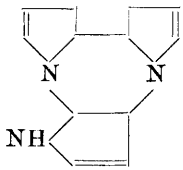


(I.)



(II.)

The last two formulæ explain the formation of indole, ammonia, and pyrrole from tripyrrole, and the formation of a salt with 1 mol. of hydrogen chloride. The presence of carbon atoms in direct combination with two nitrogen atoms, as is the case in amidines and in carbamide, would explain the ready decomposition of tripyrrole when heated at 130°, with liberation of ammonia.



(III.)

Owing to the instability of tripyrrole, no definite derivatives of it have been obtained, although it reacts in various ways. Thus, it condenses with acetone in presence of hydrochloric acid, giving a product, decomposable by ammonia with formation of a pale-yellow, crystalline compound, m. p. about 150° (decomp.), which, according to its nitrogen content and molecular weight (559), has the formula $(C_{12}H_{12}N_3)_2,(COMe_2)_3$; this compound is unstable and rapidly undergoes profound decomposition. The action of acetic anhydride on the magnesium derivative of tripyrrole at the ordinary temperature yields a bright yellow precipitate, decomposing with formation of an unstable product, which contains 9·43 % N, and gives with hydrogen chloride a brown, amorphous substance and with platinum chloride a deep red precipitate.

The action of dry hydrogen chloride on 1-methylpyrrole in benzene solution gives the *compound* $(C_4H_4NMe)_2,HCl$, which forms a white powder decomposing at about 190°, becomes yellow and then red in the air, and is analogous to the compounds obtained under similar conditions from 2-, 3-, and 2 : 3-derivatives of pyrrole.

The polymeric indoles have been studied by Keller (A., 1913, i. 403),

Scholtz (A., 1913, i, 520), and Oddo (A., 1913, i, 755). Keller's tri-indole exhibits behaviour somewhat different from that of tri-pyrrole, the former being converted quantitatively into indole when distilled in a vacuum, whereas the latter yields ammonia, indole, and pyrrole. The formula proposed by Keller for tri-indole contains three imino-groups, the fact that only one of these is capable of acetylation or benzoylation being regarded as due to steric hindrance. The author shows that the action of magnesium propyl iodide on tri-indole (1 mol.) yields 0·91—0·95 mol. of propane and suggests for tri-indole a formula analogous to formula III given above for tripyrrole. The latter formula would indicate the possibility of obtaining condensation products of the tripyrrole type from 2-, 3-, and 2 : 3-derivatives of pyrrole. Such products were not obtained under the conditions employed by Dennstedt, but they may be obtainable if these conditions are modified. T. H. P.

Aromatic Substances containing Multivalent Iodine. X. Peculiar Compounds obtained in Sandmeyer's Reaction Applied to Naphthalene Derivatives. L. MASCARELLI and G. MARTINELLI (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 25—30. Compare A., 1914, i, 267).—Diazotisation of 1-nitro-2-naphthylamine in hydrochloric acid solution and subsequent decomposition by means of potassium iodide yields: (1) 1-*chloro*-2-*iodonaphthalene* (?), $C_{10}H_6ClI$, which crystallises in white prisms, m. p. 83—84°, and (2) 1-*chloronaphthalene*-2-*diazonium chloride iodochloride*, $C_{10}H_6Cl{\cdot}N{:}NCl,ICl$, which forms shining, golden scales, m. p. 146—148° (decomp.) (compare Hantzsch, A., 1896, i, 92). The formation of such a diazonium iodochloride from the corresponding diazonium chloride is effected by the action of the iodine liberated on addition of potassium iodide, thus: $R{\cdot}N_2Cl + I_2 \rightarrow R{\cdot}N_2Cl,I_2 \rightarrow RI + N_2 + ICl$ and $R{\cdot}N_2Cl + ICl = R.N_2Cl,ICl$. That the nascent chlorine derived from decomposition of the iodine chloride is capable of replacing the nitro-group in the same way as when nitro-derivatives of naphthalene are heated with phosphorus pentachloride, is shown by the fact that 1-chloronaphthalene-2-diazonium chloride iodochloride may also be obtained by the direct action of iodine chloride on 1-nitronaphthalene-2-diazonium chloride. T. H. P.

Non-aromatic Diazonium Salts. IV. Thiazole-2-diazonium Salts. GILBERT T. MORGAN and GENEVIEVE VIOLET MORROW (T., 1915, **107**, 1291—1296).—Attempts at diazotisation of 2-aminothiazole in hydrochloric acid solution led only to the formation of tarry, amorphous products. In presence of oxyacids, diazotisation proceeded more smoothly, the best results being obtained in 20 % sulphuric acid solution, as the nitrate was too insoluble, and the perchlorate, although it readily diazotised, was explosive even in solution. Addition of sodium aurichloride to the diazotised aminothiazole in sulphuric acid gave a precipitate of thiazole-2-diazonium aurichloride, m. p. 122° (decomp.), whilst, with β-naphthol and β-naphthylamine, coppery-red flakes of *thiazoleazo-β-naphthol*, m. p. 105°, and a bluish-red *thiazole*-2-*azo-β-naphthylamine*, m. p. 135—140°, were obtained respectively.

Thiazole-2-diazonium nitrate coupled with acetylacetone giving *thiazole-2-azoacetylacetone*, golden-yellow plates, m. p. 120°. G. F. M.

Azohydroxamic Acids. I. G. Ponzio (*Gazzetta*, 1915, **45**, ii, 12—29).—From the structural analogy between ω-dinitrotoluene,

$$NO_2\cdot CPh{:}NO\cdot OH,$$

and trinitromethane, $NO_2\cdot C(NO_2){:}NO\cdot OH$, and the fact that moist ether converts the benzenediazonium derivative of ω-dinitrotoluene into ω-nitrobenzaldehyde-*p*-nitrophenylhydrazone,

$$NO_2\cdot CPh{:}NO\cdot O\cdot N_2Ph \longrightarrow NO_2\cdot CPh{:}N\cdot NH\cdot C_6H_4\cdot NO_2$$

(compare A., 1908, i, 482; 1910, i, 192), it might be expected that the benzenediazonium derivative of trinitromethane would yield dinitrocarbonyl-*p*-nitrophenylhydrazone,

$$NO_2\cdot C(NO_2){:}NO\cdot O\cdot N_2Ph \longrightarrow NO_2\cdot C(NO_2){:}N\cdot NH\cdot C_6H_4\cdot NO_2,$$

under similar conditions. The product obtained in the latter case is, however, not an isomeride, but a decomposition product of the benzenediazonium salt, namely, phenylazoformhydroxamic acid, $NPh{:}N\cdot CO\cdot NH\cdot OH$, which is the first term of a new series of compounds of special interest as regards their relation to the azides. The author considers the initial stage of this transformation to be similar to that occurring with para-substituted diazonium derivatives of ω-dinitrotoluene,

$$NO_2.CPh{:}NO\cdot O\cdot N_2ArX \longrightarrow O{:}CPh\cdot N(NO_2)\cdot N(NO)\cdot ArX$$

(compare A., 1909, i, 338, 443, 681), the whole transformation being represented by the scheme: $NO_2\cdot C(NO_2){:}NO\cdot O\cdot N_2Ph \longrightarrow NO_2\cdot CO\cdot N(NO_2)\cdot NPh\cdot NO \longrightarrow NO_2\cdot CO\cdot N{:}NPh \longrightarrow OH\cdot NH\cdot CO\cdot N{:}NPh$. Many other diazonium salts of trinitromethane give similar products. With reference to the nomenclature of these compounds, it is pointed out that true hydroxamic acids have the general formula,

$$R\cdot CO\cdot NH\cdot OH,$$

compounds of the type, $OH\cdot CR{:}N\cdot OH$, being hydroximic acids.

Phenylazoformhydroxamic acid and its analogues, when heated with aqueous alkali hydroxide, are decomposed into phenylazide [phenylazoimide], carbon dioxide, and hydrogen:

$$NPh{:}N\cdot CO\cdot NH\cdot OH \longrightarrow NPh{:}N{:}N \left(\text{or } NPh\langle{}^{N}_{N}\rangle\right) + CO_2 + H_2.$$

Since two of the three nitrogen atoms which thus unite are originally separated by a carbonyl group, this reaction is analogous to the formation of nitrogen by the action of alkaline hypochlorite on carbamide, to that of azoimide from azodicarbonamide, and to that of phenylazoimide from phenylazocarbonamide (compare Darapsky, A., 1907, i, 729). Schestakov's results (A., 1905, i, 332) render it probable that the conversion of phenylazocarbonamide into phenylazoimide proceeds according to the scheme:

$$NPh{:}N\cdot CO\cdot NH_2 \longrightarrow NPh{:}N\cdot NH_2 \longrightarrow NPh\langle{}^{NH}_{NH}\rangle \longrightarrow NPh\langle{}^{N}_{N}\rangle.$$

The transformation of phenylazoformhydroxamic acid into phenylazoimide differs, however, from these other reactions in that the intervening carbonyl group undergoes intramolecular oxidation, the use of an external oxidising agent being unnecessary. The formula ascribed to phenylazoformhydroxamic acid is supported by the fact

that this compound does not give a coloration with ferric chloride, does not form metallic salts, and is readily soluble in alkali (compare Conduché, A., 1908, i, 12, 154).

The *benzenediazonium* derivative of *trinitromethane*,

$$NO_2\cdot C(NO_2):NO\cdot O\cdot N_2Ph,$$

prepared from benzenediazonium acetate and the potassium salt of trinitromethane, forms golden-yellow prisms, and explodes with extreme violence when heated to about 40° or struck; in the impure condition it explodes spontaneously. Water decomposes it quantitatively into trinitromethane, phenol, and nitrogen, whilst 35% hydrochloric acid, previously cooled in a freezing mixture, converts it into benzenediazonium chloride and trinitromethane. The "*nitron*" salt of *trinitromethane*, $CH(NO_2)_3,C_{20}H_{16}N_4$, forms shining, golden-yellow needles, m. p. 150° (decomp.), and is practically insoluble in cold water, and very sparingly soluble in boiling water.

Phenylazoformhydroxamic acid, $C_7H_7O_2N_3$, forms flattened, white needles, with straw-coloured reflexion, m. p. 84—85°, has the normal molecular weight in freezing acetic acid, and reduces Fehling's solution and ammoniacal silver nitrate solution slowly in the cold and rapidly on heating. In concentrated sulphuric and nitric (D 1·52) acids, it forms colourless solutions, from which it is precipitated unchanged on dilution. A boiling acetic acid solution of chromic anhydride oxidises it completely, but phosphorus tri- and penta-chlorides, bromine water, acetic anhydride, and potassium permanganate in acid or neutral solution are without action. When heated with fuming hydrochloric acid in a sealed tube at 175—180°, it undergoes profound decomposition, giving phenylazoimide, aniline, and ammonia. The corresponding hydrazo-compound, NHPh·NH·CO·NH·OH, has not been obtained, reduction with either zinc dust and acetic acid or aluminium amalgam yielding only ammonia and phenylhydrazine. When suspended in absolute alcohol and treated with alcoholic potassium hydroxide, phenylazoformhydroxamic acid is immediately dissolved with generation of heat, a yellowish oil, which is readily soluble in cold alkali hydroxide, and may be phenylazoformhydroximic acid,

$$Ph\cdot N:N\cdot C(OH):N\cdot OH,$$

separating on acidification.

p-*Nitrophenylazoformhydroxamic acid*, $NO_2\cdot C_6H_4\cdot N:N\cdot CO\cdot NH\cdot OH$, forms flattened, yellow needles, m. p. 165—166°, and is obtained by nitrating phenylazoformhydroxamic acid and, in small proportion, in the decomposition of the benzenediazonium salt of trinitromethane by moist ether, when the reaction proceeds at too high a temperature, and is, consequently, too rapid. It is insoluble in the cold in alkali hydroxide solution, and in the hot is rapidly decomposed into *p*-nitrophenylazoimide, carbon dioxide, and hydrogen. T. H. P.

Formation of Azides. G. Ponzio and G. Canuto (*Gazzetta*, 1915, **45**, ii, 29—31).—The conversion of nitrosoacylarylhydrazines into acylarylhydrazines by the action of boiling water (compare Ponzio, A., 1908, i, 482; Giovetti, A., 1909, i, 738), consisting in the replacement of the nitroso-group by a hydrogen atom, should be favoured by the presence of alkali hydroxide. It is found, however, that

nitrosoacylarylhydrazines, when heated with 20% sodium hydroxide solution, undergo transformation into arylazides [arylazoimides] which can be readily isolated in consequence of their volatility in a current of water vapour: $NO\cdot NAr\cdot NH\cdot CO\cdot R \longrightarrow Ar\cdot N<\overset{N}{\underset{N}{\|}} + R\cdot CO_2H$.

This reaction furnishes a direct proof of the position assumed by the nitroso-group when acylarylhydrazines are nitrosated and indicates that arylazoimides possess the cyclic and not the open-chain structure, $NAr{:}N{:}N$; further, it is analogous to the formation of phenylazoimide from nitrosophenylhydrazine,

$$NH_2\cdot NPh\cdot NO \longrightarrow H_2O + Ph\cdot N<\overset{N}{\underset{N}{\|}},$$

but it takes place only when *R* is an aliphatic radicle.

Thus, α-nitroso-β-formyl-α-phenylhydrazine (compare Wohl, A., 1900, i, 698), when dissolved in 20% sodium hydroxide solution and distilled in a current of water vapour, yields phenylazoimide and a little aniline. α-Nitroso-β-formyl-α-*p*-bromophenylhydrazine gives *p*-bromophenylazoimide and a little *p*-bromoaniline, and α-nitroso-β-acetyl-α-phenylhydrazine yields phenylazoimide.

α-Nitroso-β-acetyl-α-p-bromophenylhydrazine, $C_6H_4Br\cdot N(NO)\cdot NHAc$, forms yellowish laminæ, m. p. 108—110° (decomp.), and gives an intense wine-red coloration with concentrated sulphuric acid. When boiled with water, it yields β-acetyl-α-*p*-bromophenylhydrazine, whilst with 20% sodium hydroxide solution it gives *p*-bromophenylazoimide.

α-Nitroso-β-benzoyl-α-phenylhydrazine undergoes some alteration, but yields no phenylazoimide when dissolved in 20% sodium hydroxide solution and distilled in a current of steam. T. H. P.

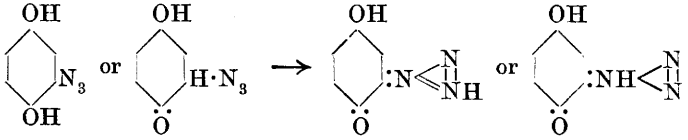
Triazoquinol. E. Oliveri-Mandalà (*Gazzetta*, 1915, **45**, ii, 120—125).—Confirmation of the structure of triazoquinol (this vol., i, 909) has now been obtained. In the form of azoimide, the triazo-group is eliminated in only minimal proportion. When the compound is gradually decomposed by means of acid or alkali, even in very dilute solution, two of the nitrogen atoms are liberated as molecular nitrogen and the third as ammonia. Such a decomposition is common with compounds which contain the grouping $\cdot CN_3{:}C(OH)\cdot$ or $\cdot CH(N_3)\cdot CO\cdot$ in a closed or open chain:

$$\cdot CH(N_3)\cdot CO\cdot \longrightarrow [\cdot CH(N<)\cdot CO\cdot \longrightarrow \cdot C(:NH)\cdot CO\cdot] \longrightarrow \cdot CO\cdot CO\cdot.$$

Triazoquinol should, therefore, yield *p*-hydroxy-*o*-benzoquinone, which cannot be isolated owing to the instability of orthoquinones, especially of those containing a hydroxyl group. As a result of this decomposition, a nitrogen-free compound, crystallising in long, red needles, m. p. above 300°, has been obtained, but has not been studied in detail.

Triazoquinol reduces ammoniacal silver nitrate solution and gives yellow and red precipitates with lead acetate and mercuric salts respectively. Its sodium and potassium salts are intensely blue, the former, $C_6H_3O_2N_3Na_2$,EtOH, being obtained by the action of very dilute sodium ethoxide (2 mols.) solution. In these highly coloured

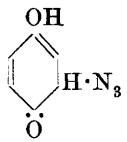
salts, the metal is probably combined with the nitrogen, the alkali causing the following change:



(compare Forster and Fierz, T., 1907, **91**, 855).

Triazoquinol forms (1) an *additive* compound with aniline, $C_6H_5O_2N_3,2NH_2Ph$, which crystallises in minute needles, decomposes at 125°, and oxidises slowly in the air; (2) a *diacetyl* derivative, $C_6H_3O_2N_3Ac_2$, which forms white needles, m. p. 115—120°, decomposes at about 140°, is stable to boiling water, and is only slightly sensitive towards diffused light, although it reddens almost immediately in direct sunlight.

Diazomethane acts on triazoquinol in two ways: (1) it etherifies the two hydroxyl groups, and (2) 2 mols. of diazomethane form an additive compound with 1 mol. of triazoquinol. Such an addition of diazomethane, which does not seem to have been observed previously, reveals the presence in the triazoquinol molecule of two ethylenic linkings and indicates the most probable constitution to be the semi-ketonic one (annexed formula). The *compound*, $C_8H_9O_2N_3,2CH_2N_2$, forms long, prismatic needles, m. p. 92°. T. H. P.



The Changes in the Physical Conditions of Colloids. XIX. Combination of Proteins with Neutral Salts. Thaddäus Oryng and Wolfgang Pauli (*Biochem. Zeitsch.*, 1915, **70**, 368—397).—The combination of proteins with potassium chloride was investigated by electrometric measurement of the changes produced in the chlorine ion concentration when dialysed proteins were added to protein solutions of varying concentrations. The technique employed was that used by Manabe and Matula in Pauli's laboratory (A., 1913, i, 1914). The chlorine ion concentration was first measured when distilled water saturated with mercurous chloride surrounded the one electrode, the other electrode being immersed in *N*-potassium chloride also saturated with the same salt. The addition of protein to distilled water caused an increase in the chlorine ion concentration, which is ascribed to the formation of a combination of the protein with the mercury salt. Measurements were then made of the chlorine ion concentrations of potassium chloride solutions of varying concentration, alone and in presence of proteins, the solutions being always saturated with mercurous chloride. After corrections have been made for the action of the protein on the mercury salts, the changes in the chlorine ion concentrations of the potassium chloride solutions produced by the addition of the proteins (serum, serum albumin, gelatin, and deaminogelatin) are calculated from the results of the electrometric measurements. The authors draw the conclusion that there is a combination of the protein with the salt, the possible nature of which is discussed in some detail. Similar results were obtained with glycine and

alanine as with the proteins; carbamide, however, gave no indications of any salt combination, as it did not materially influence the chlorine ion concentrations of the potassium chloride solutions. S. B. S.

Proteins. Can a Protein be Completely Hydrolysed by Successive Digestion with Pepsin, Trypsin, and Erepsin? A. C. ANDERSEN (*Biochem. Zeitsch.*, 1915, **70**, 344—367).—The author draws the conclusion that it is impossible completely to degrade proteins by successive treatments with pepsin, trypsin, and erepsin. This statement is illustrated by numerous experiments, and it is shown that after prolonged treatment with ferments, the number of amino-groups and amount of ammonia can be increased by subsequent hydrolysis by acids. The methods of van Slyke and Sörensen (formaldehyde titration) were employed in the investigation, and their relative merits are discussed. S. B. S.

The Hydration of the Protein Ion. WO. PAULI (*Biochem. Zeitsch.*, 1915, **70**, 504).—A claim for priority as to the conception of the hydrated protein ion. S. B. S.

Proteins. II. The Combination of Ammonia in the Proteins. A. C. ANDERSEN and REGITZE ROED-MÜLLER (*Biochem. Zeitsch.*, 1915, **70**, 442—463).—Some experiments are described which tend to indicate the existence of uramic acids in the protein molecule. S. B. S.

The Kyrine Fraction Obtained on Partial Hydrolysis of Proteins. II. P. A. LEVENE and J. VAN DER SCHEER (*J. Biol. Chem.*, 1915, **22**, 425—432. Compare A., 1913, i, 109).—The kyrine obtained by the partial hydrolysis of casein has been separated into two fractions, one of which gave a precipitate with silver nitrate whilst the other did not, and then these fractions have each been subdivided into soluble and insoluble phosphotungstates. The fraction which gave no silver precipitate but an insoluble phosphotungstate, was converted into a crystalline *sulphate*, $C_{16}H_{32}O_9N_4S$, which was crystallised until the ratio amino-nitrogen to total nitrogen was constant at 50·5 to 100. This contained all the basic nitrogen in the form of an amine, and lysine was separated as the picrate, quantitatively, from the products of complete hydrolysis. The substance was, therefore, most probably a tripeptide containing lysine, valine, and oxyproline, although the isolation of the amino-acids was not successfully accomplished. Casein-kyrine, like gelatin-kyrine, can therefore be separated into simple peptides, each of which contains only one basic substance in the molecule. J. C. W.

Optical Properties of Protein and Certain Other Substances. I. (*continued*). M. A. RAKUZIN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1050—1054. Compare *ibid.*, 144).—In determining the specific rotation of the albumin of hens' eggs, it is necessary to apply corrections for the proportions of ash and of fat or extractive matters present. The composition of the egg-albumin is: ash,

0·41—0·60%; fat, 0·20—0·23%; albumin, 14·26—15·34%; water, 83·84—85·04%. The ash has the following percentage composition: K_2O, 30; Na_2O, 30; Cl, 25—30; P_2O_5, 4—5; SO_3, 1—2; MgO, 2—2·5; CaO, 2—2·5; Fe_2O_3, 0·4—0·6; SiO_2, 1. For a series of albumins from seven different eggs, the value of D^{15} varies from 1·0425 to 1·0515, and for three different samples of albumin, the value of $[\alpha]_D$ lies between $-36·4°$ and $-37·1°$ (compare Panormov, A., 1899, i, 655). From a 50% solution of the albumin, alumina adsorbs 19·22% of the total albumin, the values of $[\alpha]_D$ for the adsorbed and non-adsorbed fractions being $-56·0°$ and $-32·6°$ respectively; the fat is entirely adsorbed and the ash entirely unadsorbed by this means. The fraction of the albumin remaining in the solution after the adsorption is not affected by a second treatment with alumina. In 50% solution, the crude albumin is adsorbed negatively by gelatin amounting to 3% of the weight of the solution, the values of D^{19} and $(\alpha)_D$ being increased from 1·0169 and $-2·6°$ to 1·0193 and $-3·8°$ respectively. Both the original albumin and its adsorption fractions have amorphous structures. The properties of the adsorbed fraction, and the character of the adsorption, whether reversible or irreversible, are under investigation. T. H. P.

Preparation and Composition of Caseinogen. JOHN MELLANBY (*Biochem. J.*, 1915, **9**, 342—350).—Caseinogen precipitated from milk by alcohol, forms a milk-white solution in water with all its original properties. It is a complex of protein and calcium phosphate, 3,500 grams of caseinogen containing approximately a gram-molecule of tricalcium phosphate. In acidic caseinogen there is 1 gram atom of phosphorus per 3,400 grams of caseinogen. 6 Gram-molecules of acetic acid (equivalent to 1 gram-mol. of calcium phosphate) precipitate acidic caseinogen from approximately 3,500 grams of caseinogen. This suggests that its protein unit has an approximate weight of 3,400, that caseinogen consists of 1 unit of protein and a molecule of the phosphate, and that the precipitation by acetic acid may be expressed thus:—Protein $Ca_3(PO_4)_2 + 6H\bar{A} =$ Protein $6H\bar{A} + Ca_3(PO_4)_2$. The following relation of the protein to the phosphate is suggested: $R<^{(NH_2)_2Ca_2H_2(PO_4)_2}_{XCa}$, where the group X has feeble acidic properties. W. D. H.

Changes in the Physical Conditions of Colloids. XV. The Caseinogenates. WOLFGANG PAULI (*Biochem. Zeitsch.*, 1915, **70**, 489—503).—The observations of Laqueur and Sackur of the increase of the viscosity of caseinogen solutions, with increasing concentration of alkalis, up to a certain maximum which is followed by a decrease, is confirmed. It is shown, however, that this statement only holds true of the initial values, for if the solutions are kept, the viscosity decreases, and the rate of decrease is more rapid in the solutions containing the larger amounts of alkali, so that after about one hour, there is no great difference in the viscosity of the solutions with different amounts of alkali.

Measurements were also made of the electrical conductivities of the

alkali salts. The mobility of the caseinogen ion was found to increase with increasing alkali concentration, indicating the formation of multivalent caseinogen ions. The differences between the conductivities of the sodium potassium and ammonium salts were also measured. The difference in λ between the potassium and sodium salts for equivalent concentrations was found to be 14, which is less by 6 or 8 units than the differences for salts of other acids as found by Kohlrausch and Holborn, which fact the author takes to indicate that 70—80% of the caseinogen is combined with alkali in the form of a typical salt.

Measurements of the depressions of the freezing points of solutions of caseinogen are also recorded. S. B. S.

Rotatory Powers of Caseinogenates of the Alkali Metals. M. A. Rakuzin and (Mlle.) R. S. Logunova (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1059—1061).—In aqueous solution, the alkali caseinogenates, which are neutral to phenolphthalein, have the following values of $[\alpha]_D$: lithium, $-114{\cdot}28°$; ammonium, $-129{\cdot}85°$; sodium, $-145{\cdot}36°$; potassium, $-156{\cdot}62°$. Thus, the specific rotation increases with the atomic weight of the metal. The only known case analogous to this is that of petroleum fractions, the specific rotation of which increases with the specific gravity. The salts of aspartic acid, leucine, and tyrosine are being examined in this direction. T. H. P.

Indole Content of the Digestion Products of Fibrin and Casein. W. von Moraczewski (*Biochem. Zeitsch.*, 1915, **70**, 37—44).—The proteins were submitted to peptic, then to tryptic digestion, and the digestion products were then allowed to undergo putrefaction after infection with human fæces. The indole formed was distilled off in steam, and the indole estimated colorimetrically by means of the nitrite reaction. It was found that the caseoses yielded more indole than the residual paranuclein. S. B. S.

The Affinities of Hæmatin. J. A. Menzies (*J. Physiol.*, 1915, **49**, 452—456).—Spectroscopic evidence shows that hæmochromogen and globin reunite to form hæmoglobin, provided that the hæmatin from which the hæmochromogen is prepared has not been precipitated. Attempts to combine precipitated hæmatin or hæmochromogen prepared from it with various proteins and amino-acids failed. W. D. H.

Nitrated Proteins. III. Conversion of Fibroin into Nitrofibroin (Fibroinxanthoproteic Acid). Treat B. Johnson, Arthur J. Hill, and Leon P. O'Hara (*J. Amer. Chem. Soc.*, 1915, **37**, 2170—2178).—An account is given of a study of the nitration of silk fibroin with nitric acid (D 1·12) at a uniform temperature (18—25°). It has been found that the action of the acid proceeds gradually until after eight days about 30% of the fibroin has been dissolved. The remainder forms an orange-coloured powder which is very resistant to further action of the acid. After the action has

continued for twenty-four hours, the nitrated protein fails to respond to Millon's test, although the reaction is far from complete. This may possibly indicate that the tyrosine nucleus of the fibroin is wholly converted in twenty-four hours into a dinitro-compound. From 20 grams of fibroin about 14·3 grams of the insoluble nitration product were obtained containing 18·0% of nitrogen. This nitrofibroin begins to darken at about 240°, and becomes almost black at 300°; its behaviour with various reagents is compared with that of the original fibroin. E. G.

Some Products of Hydrolysis of Gliadin, Lactalbumin and the Protein of the Rice Kernel. THOMAS B. OSBORNE, DONALD D. VAN SLYKE, CHARLES S. LEAVENWORTH, and MARIAM VINOGRAD. (*J. Biol. Chem.*, 1915, **22**, 259—280).—Gliadin is not free from lysine, but contains 0·64 % when estimated as picrate; the percentage is still higher (1·2%) when estimated by the partition of nitrogen by the van Slyke method. By the same methods the histidine content is 1·84 ± 0·35, and the arginine 2·84 ± 0·14%. The amount of ammonia nitrogen corresponds closely with that required for amide union with one carboxyl group of the glutamic and aspartic acids, and this is evidence that the ammonia is in acid-amide form as in asparagine and glutamine. In all three proteins the free amino-nitrogen is equal to one-half of the lysine nitrogen estimated by van Slyke's method. The hexone base content of lactalbumin was as follows: lysine, 9·16 ± 0·68; histidine, 2·06 ± 0·54; and arginine, 3·23 ± 2·3%; the upper limit is by van Slyke's, the lower by Kossel's method. In oryzenin, the chief protein of rice, there is a greater yield of each hexone base than in the main protein of wheat and maize, and but little ammonia and non-amino-nitrogen. It more nearly resembles animal proteins in general make-up, and this may explain the extensive use of rice in certain countries, in spite of its low protein content. W. D. H.

Rotatory Powers of Aqueous Solutions of Albumin-Peptone and their Adsorption by Alumina. M. A. RAKUZIN and (MLLE.) EK. MAKS. BRAUDO (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1057—1059).—Albumin-peptone, $[\alpha]_D$ − 95·24°, is resolved by alumina into an adsorbed portion (24·19%) having $[\alpha]_D$ − 156·68° and a non-adsorbed portion, $[\alpha]_D$ − 75·0°. The latter remains unchanged when its solution is subjected to further treatment with alumina. The adsorption is irreversible. T. H. P.

The Chemical Nature of Certain Enzymes. TH. BOKORNY (*Biochem. Zeitsch.*, 1915, **70**, 213—251).—A series of experiments is described, which show, according to the author, that ferments combine with acids and bases. Pepsin is an exception and combines with neither, and diastase combines only with bases. The conclusion is drawn that the enzymes generally are protein-like substances. S. B. S.

Adsorption of Aqueous Solutions of Pepsin by Alumina. M. A. RAKUZIN and (MLLE.) EK. M. BRAUDO (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1055—1056).—Whereas trypsin is optically inactive and is

not adsorbed from its solutions by alumina, pepsin exhibits the specific rotation, $[\alpha]_D$ +68·0°, and is adsorbed by alumina. From 100 grams of a 5% aqueous pepsin solution (D^{15} 1·0222), 10 grams of alumina adsorbs, in twenty-four hours at the ordinary temperature, 12·4% of the pepsin present, the fraction thus removed having $[\alpha]_D$ +68·0°. If the liquid is then freed from alumina by centrifugation and treated with a second portion of alumina, the concentration and optical rotation of the solution remain unchanged. Removal of the liquid by pressure from the alumina containing the adsorbed pepsin, and treatment of the residue with water yield a neutral liquid which is proteolytically inactive, and leaves no solid residue on evaporation. Adsorption of pepsin from its aqueous solution by means of alumina is, therefore, an irreversible process.

T. H. P.

Optical and Certain Other Properties of Trypsin. M. A. Rakuzin and G. D. Flier (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1048—1049).—Trypsin (Merck) forms optically inactive aqueous solutions, and its appearance under a polarising microscope shows it to be amorphous. The preparation examined contained 3·09% of free hydrochloric acid. After neutralisation by means of sodium hydroxide, its solution exhibited no adsorption in presence of alumina. Negative adsorption of trypsin proceeds normally, the value of D^{16} for a 3·9% solution being increased from 1·0152 to 1·0217 when left for twenty-four hours in contact with 3% of gelatin (compare this vol., i, 324). T. H. P.

The Proteoclastic Action of the Degradation Products of the Proteins. Proteoclasis by Dialysates of Trypsin Digests; Action of the Bile Salts of the Alkali Metals; Conditions for Solution of Proteins. E. Herzfeld (*Biochem. Zeitsch.*, 1915, **70**, 262—268).—From experiments carried out by the dialysis method and the quantitative ninhydrin reaction of the author, the conclusion is drawn that the reactive part of trypsin passes into the dialysate through a parchment membrane, the residue in the membrane being almost inactive. Aliphatic amino-acids have a larger degradative action than the aromatic acids. Experiments are also described which tend to show, according to the author, that bile salts can exert a digestive action on fibrin. A theory is also put forward to explain the process of solution of protein coagula, according to which a partial scission of certain groups must take place, and the degradation products maintain the coagulum in a colloidal state of solution. S. B. S.

Urease, an Enzyme Present in Soja Beans. K. R. Labberté (*Pharm. Weekblad*, 1915, **52**, 1428—1440).—A study of the hydrolysis of carbamide by urease, with production of ammonium carbonate. The reaction is not unimolecular, and its velocity is proportional to the concentration of the enzyme. The reaction is retarded by the product formed, but is suitable for the estimation of urea. Ferrous sulphate, sodium sulphate, and hydrogen

sulphide retard the hydrolysis, but the action of hydrogen sulphide is less inhibitory than that of the other two substances. The enzyme does not hydrolyse acetamide. A. J. W.

Enzymes: Synthetic and Hydrolytic Hydroxynitrilase. II. VERNON K. KRIEBLE (*J. Amer. Chem. Soc.*, 1915, **37**, 2205—2213).—Rosenthaler (A., 1913, i, 410, 411, 663) has stated that emulsin seems to contain two distinct enzymes, one of which effects the synthesis of benzaldehydecyanohydrin whilst the other causes its hydrolysis. Experiments are now described in which the rate of reaction and the equilibrium point between hydrogen cyanide and benzaldehyde were determined in presence of hydroxynitrilase in order to ascertain whether there was any difference in the enzyme obtained from various sources, and also in the enzyme obtained from the same source but by various methods and subjected to different treatment. If there is a synthetic and hydrolytic enzyme for a certain reaction, there must be a difference in the equilibrium point, but no variation in the equilibrium point in the synthesis of mandelonitrile was observed in any case. No evidence could be obtained of the possibility of effecting the separation of a hydrolytic from a synthetic enzyme in a preparation of hydroxynitrilase when treated by the methods suggested for the purpose by Rosenthaler. E. G.

The Mechanism of the Natural Formation of Lactic Acid. CARL NEUBERG and JOH. KERB (*Biochem. Zeitsch.*, 1915, **71**, 245—254).—The authors are unable to confirm the results of Dakin and Dudley (A., 1914, i, 227, 342), according to whom the ferment which causes conversion of methylglyoxal into lactic acid ("glyoxylase," or, to use the name given by the authors, "ketone aldehyde mutase"), differs from the aldehyde mutase of Parnas. They are unable to confirm the statement that only the "glyoxylase" of Dakin and Dudley is inhibited in its action by pancreatin.

The authors reply to certain criticisms of their views on lactic acid formation by M. Oppenheimer (A., 1914, i, 363). S. B. S.

Reductase. IV. The Influence of Alkaloidal and Other Narcotic Poisons on Reductase. DAVID FRASER HARRIS and HENRY JERMAIN MAUDE CREIGHTON (*J. Biol. Chem.*, 1915, **22**, 535—545).—Chloroform inhibits the action of reductase more than do ether or alcohol; it is much more effective than many virulent poisons; substances like aconitine and hyoscine hydrobromide inhibit reductase no more effectively than substances such as caffeine, which are less poisonous to protoplasm. The deadly power of narcotic alkaloids would seem to be exerted against some physiological activity of the cellular mechanism other than the inspiratory phase of tissue respiration (action of reductase). The methods used were the same as in the authors' previous work. W. D. H.

The Phosphatases of Malt. LUDWIG ADLER (*Biochem. Zeitsch.*, 1915, **70**, 1—36).—There are in malt at least two kinds of phos-

phatases, one of which brings about the solution of insoluble organic phosphate complexes, whereas the other influences the formation of inorganic phosphates. The temperature optimum for the phosphatases is about 58°; above this temperature their activity rapidly diminishes. In the extract of malt which has been kept for five hours, the enzyme causing the solution of the organic phosphate complex has lost its activity, whereas that producing the scission of inorganic phosphate retains its activity for fourteen hours. The activity depends largely on the concentration of the solutions, as a high viscosity and the presence of scission products (inorganic phosphates) have a deleterious influence. An extract of 1 part of malt in 20 parts of water gives the best results; in more dilute solutions, the formation of inorganic phosphates diminishes. The hydrion concentration is also of great importance; when $p_H = 5{\cdot}4$, the total phosphoric acid of malt can be rendered soluble, 93% of which will be found in the form of inorganic phosphate; the phosphatases are still more sensitive to the hydroxyl ion concentration, but they are still active in a relatively acid solution; when $p_H = 2{\cdot}0$, the phytin passes into solution. For the destruction of the phosphatases by alcohol, a somewhat drastic treatment is necessary; it is best accomplished by heating with 85% alcohol. This treatment forms the foundation of a method for the determination of the pre-existing phosphates in malt. The phosphatases are secretion enzymes which exert their activity outside the cell. The phytase is a phosphatase which plays an important part in the reaction, and acts on commercial phytin preparations. S. B. S.

Physiological Chemistry.

The Physico-chemical Regulation of Respiration. HANS WINTERSTEIN (*Biochem. Zeitsch.*, 1915, **70**, 45—73).—Experiments were made by infusion of hydrochloric, sulphuric, phosphoric, acetic, lactic and carbonic acids, and of alkalis into the blood of rabbits narcotised with chloral hydrate, and the changes in the pulmonary ventilation, the [H$^{\cdot}$] concentration, and carbon dioxide tension of the blood were measured. It was found that the changes in the pulmonary ventilation ran parallel with the changes produced in the [H$^{\cdot}$] concentration of the blood, whereas the alteration in the carbon dioxide tensions were somewhat irregular. It is claimed that the results confirm the "reaction theory" of the author, according to which carbon dioxide is not a specific stimulant of respiration, but acts by altering the hydrion concentration of the blood, thus chemically controlling the respiration, which in its turn tends to keep the reaction of the blood constant. S. B. S.

The Rôle of Oxydases in Respiration. G. B. Reed (*J. Biol. Chem.*, 1915, **22**, 99—111).—Lillie (A., 1913, i, 1124), who studied the formation of indophenol under the influence of intracellular oxidation, came to the conclusion that biological oxidations are chiefly due to electrical processes operating in the neighbourhood of the nuclear and plasma membranes. The author has repeated Lillie's experiments, using plant (particularly the lower epidermis of onion-bulb leaves) and animal material. He finds that the oxidation of a mixture of α-naphthol and *p*-phenylenediamine to indophenol frequently proceeds most rapidly in the region of semi-permeable membranes, that many nuclear and all the plastid surfaces show no activity, and that the oxidation is not prevented by rupturing the membranes, but is entirely stopped by agents which kill oxydases. The rôle of oxydases is, therefore, much more important than the supposed electrical phenomena. J. C. W.

The Effect of Alkalis on the Rates of Oxidation and Reduction in Blood. Toyojiro Kato (*Biochem. J.*, 1915, **9**, 393—411).—Alkali hastens oxygenation and slows reduction in blood. At body temperature, *M*/200NaOH lessens the velocity of reduction to 0·78, and raises that of oxidation to 1·25 of the original values; one is nearly the reciprocal of the other. This increases with increased concentration up to *M*/50. In equimolecular concentrations, sodium hydroxide and carbonate have an equivalent effect; the effect of disodium hydrogen phosphate and sodium hydrogen carbonate is less. The effect of carbon dioxide in the oxidising gas in the proportion found in alveolar air is counteracted by concentrations of alkali between *M*/200 and *M*/100. In the same species of animal the rates are generally similar in different animals, but there are exceptions. In different species the rates vary.

W. D. H.

Experimental Glycosuria. IX. The Blood-sugars of the Dog under Laboratory Conditions. J. J. R. Macleod and R. G. Pearce (*Amer. J. Physiol.*, 1915, **38**, 415—424).—The sugar content of portal and vena cava blood exhibits very little difference in most cases. An increase in the systemic blood does not immediately produce a similar increase in the portal vein. The excess is retained somewhere, probably in the muscles. If dextrose is injected into the portal vein, this delay is not noticed. Possibly sugar set free in the liver by hyperglycogenolysis is more liable to be fixed or used by the tissues than injected dextrose. During anæsthesia, the sugar level varies, but in the course of ten minutes these variations are small as compared with those seen in animals in which the splanchnic or hepatic nerves are stimulated.

W. D. H.

The Behaviour of the Sugar of the Blood after Venesection. Ernst Hirsch (*Biochem. Zeitsch.*, 1915, **70**, 191—212).—A technique is described by means of which large amounts of blood may be withdrawn from rabbits with the minimal amount of psychic

excitation. A single withdrawal of 50 c.c. from a healthy, well-nourished animal was found to be practically without effect on the content of blood-sugar. Repeated withdrawal of large quantities caused an increase in the amount of sugar until values of 0·24—0·31% were attained. The amount depends rather on the withdrawal of large amounts at one time than on the number of withdrawals, as repeated withdrawals of small amounts, even when the total reached 118 c.c., did not result in hyperglycæmia. The return to normal conditions follows rapidly (in two to three hours) after venesection, the highest value being generally attained in about forty-five minutes. An animal which has been weakened and rendered anæmic by previous letting of blood readily reacts to a single withdrawal of a large quantity, with appreciable rise in the blood-sugar. Animals which have fasted for five to six days also react to a withdrawal of blood, but the reaction is apparently somewhat less than that of well-nourished animals. After a diet rich in carbohydrates, the hyperglycæmia due to withdrawal of blood follows very readily, and is often accompanied by glycosuria. The experiments indicate, generally, that the stimulus causing hyperglycæmia is the withdrawal of blood. S. B. S.

The Part Played by the Different Blood-elements in Glycolysis. Hugh Maclean and Henry Bright Weir (*Biochem. J.*, 1915, **9**, 412—419).—The white cells are much more active in glycolysis than the red; the ratio of activity varies from 200: to 1000:1. In leucæmia, glycolysis is more marked than in normal blood. In normal blood, the small number of white cells has a greater influence than the more numerous red corpuscles. W. D. H.

The Dextrose and Diastase Content of the Blood as Affected by Ether Anæsthesia of Animals Fed on Different Diets. Ellison L. Ross and Hugh McGuigan (*J. Biol. Chem.*, 1915, **22**, 407—416).—Ether anæsthesia causes hyperglycæmia, which is greater in dogs fed on a meat diet than when the diet includes carbohydrate. The ether itself, and not asphyxia or excitement, is responsible for the greater part of the hyperglycæmia. Ether anæsthesia does not increase the diastatic power of blood-serum, but the diastase concentration is increased by a pure meat diet. W. D. H.

The Estimation of Non-protein Nitrogen and Dextrose in Finger-blood. Alonzo E. Taylor and Florence Hulton (*J. Biol. Chem.*, 1915, **22**, 63—69).—The non-protein nitrogen is estimated by a modification of the Folin method which can be applied to small amounts of blood, and sugar by Bang's method. Full details and precautions are given. Considerable fluctuations in both are found in health. W. D. H.

The Urinary and Blood Nitrogen Curves after Feeding. O. H. Perry Pepper and J. Harold Austen (*J. Biol. Chem.*, 1915, **22**, 81—86).—The daily variation in the non-protein blood nitrogen

of the dog on a diet containing 0·4 gram of nitrogen per kilo. is about 9 mg. The maximum occurs two hours after a meal, and the normal level is reached eight to twelve hours later. After excessive feeding with meat that figure may reach 25—40 mg. in six to eight hours, and the original level is not reached within twenty-four hours. In one case, presumably of slow absorption, the maximum was slowly reached in fourteen hours, and the urinary nitrogen ran a parallel course. Although the urinary and blood curves are usually parallel, the blood nitrogen may exhibit a second rise when the urinary excretion is falling. In fasting, there is a gradual fall in the blood curve to 12—18 mg. for thirty to forty-eight hours; in the next few hours it rises to 25—28 mg., at which it persists. The curve of the urinary nitrogen is similar, but less pronounced. The amount of urine influences the urinary nitrogen much more when the nitrogen values are high than when they are low. Ambard's formula fails to give a constant figure, and no formula was found to express accurately the relation between blood nitrogen, urinary nitrogen, and the amount of urine. W. D. H.

The Relation of Salivary to Gastric Digestion. Leslie Algernon Ivan Maxwell (*Biochem. J.*, 1915, **9**, 323—329).—Peptic digestion is delayed in the presence of colloidal starch solution through adsorption of enzyme; a 2% solution increases the time fourfold. Between the amylodextrin and erythrodextrin stage of disruption of the starch molecule, the power to adsorb pepsin is lost. Unboiled starch does not hinder peptic digestion, but all cooked farinaceous foods do unless first subjected to salivary digestion. Gum acacia inhibits peptic activity, and here saliva has no effect. W. D. H.

Acidity of Undiluted Normal Gastric Juice from a Case of Human Gastric Fistula. M. L. Menten (*J. Biol. Chem.*, 1915, **22**, 341—343).—In this specimen the estimation was made, not by titration, but by the more accurate gas-chain method. The results, however, agree closely with those of Carlson and of Pavlov (in dogs) by the older method. W. D. H.

Reaction of the Pancreas. J. H. Long and F. Fenger (*J. Amer. Chem. Soc.*, 1915, **37**, 2213—2219).—All the work published hitherto on the subject of the pancreatic juice has shown that it has a more or less alkaline reaction. The pancreatic juice employed in all those investigations, however, has been a secretion usually obtained by means of a permanent or temporary fistula.

It has now been found that if the pancreas of the ox, hog, or sheep is cut open and tested with litmus paper immediately after the death of the animal, a distinct acid reaction is always observed. The press juice can be separated from the minced pancreas by means of a centrifugal machine. In this operation, the minced mass becomes divided into three layers, the lowest layer consisting largely of protein, the uppermost layer of solid, containing much

fat, and the intermediate layer of a clear liquid. The liquid layer has an acid reaction, which seems to be due to the presence of sodium dihydrogen phosphate. This reaction is nearly constant in the case of the liquid from ox and hog pancreas; it is as characteristic as that of the blood, and may be expressed approximately by the relation $C_H = 29 \times 10^{-7}$. E. G.

Digestive Activity and Composition of Different Fractions of the Pancreas. J. H. Long, Mary Hull, and H. V. Atkinson (*J. Amer. Chem. Soc.*, 1915, **37**, 2427—2430).—Long and Fenger (preceding abstract) have shown that minced pancreas tissue can be divided into three different layers by centrifugal action. The composition and digestive activity towards starch and fibrin have been determined of the three layers obtained from the pancreas of the hog, ox, and sheep. The results show that in each case the three fractions have different properties, especially with respect to the distribution and amount of the ferments present. E. G.

Formaldehyde Micro-titration and its Applications in Physiology. I. General. II. Study of Peptidolytic Enzymes. A. Clementi (*Atti. R. Accad. Lincei*, 1915, [v], **24**, ii, 51—55, 102—107).—When a 1 c.c. burette divided into 200 parts and a $N/50$-sodium hydroxide solution are employed, Sörensen's "formaldehyde" titration may be applied to the investigation of less than 0·001 gram of an amino-acid. The author has estimated in this way glycine, leucine, *dl*-leucylglycine, and glycocyamylglycine, 10—20 c.c. of a $N/1000$-solution of the amino-acid or polypeptide and 1 c.c. of formaldehyde solution being titrated with $N/50$-sodium hydroxide solution in presence of phenolphthalein; the alkali is added until the distinct red colour of Sörensen's second stage appears. Glycocyamylglycine behaves as a neutral compound under these conditions.

The method has been applied to the study of the action of pancreatic juice and of aqueous extracts of liver and muscle on *dl*-leucylglycine in presence of toluene. The variations in the proteolytic actions of extracts of the muscles of different animals observed by Abderhalden and Teruuchi (A., 1906, ii, 873) may be determined or influenced by the presence or absence of blood in the muscular tissues employed. T. H. P.

Animal Calorimetry. XII. The Influence of the Ingestion of Fat. J. R. Murlin and Graham Lusk (*J. Biol. Chem.*, 1915, **22**, 15—41).—After feeding with fat, the greatest influx of fat globules occurs during the sixth hour; heat production reaches its maximum at the same time, and falls to its basal level four hours later. It does not affect the heat produced from protein and glycogen. If dextrose is given at the height of heat production, a second increase in heat development occurs equal to that which the dextrose given alone would have caused; if glycine is further added, the total increase in metabolism is very nearly equal to the sum of the increases which each of the three materials would have induced alone. W. D. H.

Absorption of Fat from the Mammalian Stomach. LAFAYETTE B. MENDEL and EMIL J. BAUMANN (*J. Biol. Chem.*, 1915, **22**, 165—190).—In spite of histological evidence of fat in the stomach walls, when fat is given, the transport to the blood or lymph is apparently nil, or minute and slow. No increase in the fat of the blood or lymph could be detected, although the methods used easily detected the fat in these fluids after intestinal absorption.

W. D. H.

The Assimilation of Cholesterol and its Esters. J. HOWARD MUELLER (*J. Biol. Chem.*, 1915, **22**, 1—9).—Cholesterol is readily absorbed from the intestine, and may be found in the thoracic duct. If free cholesterol is given, part is esterified during absorption; if esters are given, part appears as free cholesterol; the ratio remains approximately constant in the chyle, and is not affected by the presence of small quantities of fatty acids in the food.

W. D. H.

The Metabolic Relationship of Proteins to Dextrose. II. Formation of Dextrose from Body Proteins. N. W. JANNEY and F. A. CSONKA (*J. Biol. Chem.*, 1915, **22**, 203—213).—In the fasting phloridzin diabetic dog, the D:N ratio is 3·4:1 rather than 3·67:1 (Lusk). The body proteins of the dog collectively yield in metabolism about 57·5% of dextrose, corresponding with a ratio 3·6:1. In the rabbit the ratio is 3·8:1. The calculated yield of 45% dextrose is incorrect. W. D. H.

Rate of Metabolism of Proteins and Amino-acids. N. W. JANNEY (*J. Biol. Chem.*, 1915, **22**, 191—192).—The rate of protein metabolism is nearly identical with that of amino-acids, the time required being but little longer than that of the absorption followed by the excretion of dextrose. W. D. H.

Protein Metabolism after Repeated Hæmorrhage. A. E. TAYLOR and H. B. LEWIS (*J. Biol. Chem.*, 1915, **22**, 71—75).—After repeated venesections in dogs, there is a progressive decrease in total nitrogen and total protein in the blood, but a large increase in non-protein nitrogen, both in the urea and more especially in the amino-acid fractions. This must be derived either from the hydrolysis of tissue- or blood-protein, or more probably from a setting free of amino-acids previously stored in the tissues. W. D. H.

Protein Minima for Maintenance. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with EDNA L. FERRY and ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1915, **22**, 241—258).—The present experiments are made, as in previous work by the authors, on rats. The results are summarised in tables. The different proteins used (lactalbumin, caseinogen, edestin, milk-proteins, and gliadin) are not so widely different in their general amino-acid make-up as to lead to wide differences of protein minimum requirement. But in the case of growth, the divergences manifest themselves more conspicuously than in mere maintenance. The appar-

ently greater efficiency of lactalbumin in contrast with the others is in harmony with the observations relating to the economy of this protein as a supplement to deficient rations. W. D. H.

The Relative Amounts of the Different Lipoids of the Brain in Dogs which have Acquired a Tolerance to Morphine. JOHANNES BIBERFELD (*Biochem. Zeitsch.*, 1915, **70**, 158–163).—The estimation of certain lipoid constituents in the brain of dogs which had acquired a tolerance for morphine revealed no marked deviation from the normal. S. B. S.

The Death Temperature of Nerve. W. D. HALLIBURTON (*Quart. J. expt. Physiol.*, 1915, **9**, 193—198).—When a nerve is heated beyond a certain temperature, excitability, conductivity, and the electrical "sign of life" are lost together. This temperature is identical with that at which the first protein in the series contained within nerve-protoplasm enters into the condition of a heat-coagulum. With fairly rapid heating, the death temperature in frogs' nerve is 40—41°, but prolonged exposure to temperatures below this effects the same result. The lowest temperature used, 36·5°, accomplishes this in a little more than an hour. This is exactly parallel to what happens when a nerve is heated, or an extract of nerve; in the former case, shortening begins at about 36°, but is not energetic until 40° is reached, but full shortening can be obtained at the lower temperature if time is allowed; in the latter case, opalescence, the initial sign of coagulation, sets in at 36°, and if the heating is prolonged, formation of flocculi occurs, just as it does at 40° in less time. In warm-blooded animals, the death temperature is higher, and is there also identical with the coagulation temperature of the first of the proteins in this variety of nerve. Miram and also Hafeman (A., 1908, ii, 513) place the death temperature of frogs' nerve higher; this result is quite inexplicable. W. D. H.

Absorption of Iron from the Organs after Hæmolysis. ROBERT MUIR and JOHN SHAW DUNN (*J. Path. Bact.*, 1915, **20**, 41—49).—After acute hæmolytic anæmia in rabbits, the excess of iron which had been stored in the organs was nearly all absorbed by the time of complete regeneration of the blood, and presumably utilised for blood-formation. The absorption is most complete from the liver cells. It is less complete, a certain excess still remaining in the endothelium of the liver capillaries, in the spleen pulp, and especially in the kidney cortex. W. D. H.

The Influence of Proteins and Protein Degradation Products on the Formation of Glycogen in the Surviving Liver of the Tortoise; the Function of the Liver in the Elaboration of Proteins and their Degradation Products. HENRY B. RICHARDSON (*Biochem. Zeitsch.*, 1915, **70**, 171—190).—The experiments were carried out by means of Grube's technique. It was found that the addition of peptone to Ringer's solution, employed for the

perfusion of the liver, inhibited the formation of glycogen. The same result was obtained by the addition of hydrolysed caseinogen. Ereptone was without effect, and this is possibly due to the fact that it contains both stimulatory and inhibiting substances. A mixture of glycine, leucine, *d*-alanine, and *l*-valine was without effect on glycogen formation, whereas glutamic acid exerts an inhibitory action. S. B. S.

Experimental Glycosuria. X. The Sugar-retaining Power of the Liver in Relation to the Glycogen already in that Organ. J. J. R. Macleod and R. G. Pearce (*Amer. J. Physiol.*, 1915, **38**, 425—437).—The existing glycogen content of the liver does not demonstrably influence the rates with which this organ removes dextrose from the blood of the portal vein. W. D. H.

The Predominance of the Liver in the Formation of Urea. A. E. Taylor and H. B. Lewis (*J. Biol. Chem.*, 1915, **22**, 77—80).—The view that the liver is all-important in urea formation is based largely on circumstantial evidence. In the present experiments on four dogs, the whole alimentary tract was removed, so that the liver was supplied only by the hepatic artery. The non-protein nitrogen in the blood from the liver is a little greater than in that from the hind legs, but the slight excess of urea in the former, even allowing for creatine from the leg muscles, is not regarded as in favour of the view that the liver has a predominant action in urea formation. W. D. H.

Autolysis. II. The Acceleration of Liver Autolysis. H. C. Bradley (*J. Biol. Chem.*, 1915, **22**, 113—123).—Caseinogen, peptone, and coagulated liver-proteins are digested by the autolytic enzymes of the liver: their addition gives the same type of acceleration as does manganous chloride; this salt does not increase the rate of digestion of caseinogen or peptone, and so cannot act as an activator or co-enzyme. Edestin is not digested unless manganous chloride is added, and egg-albumin is not digested even in its presence, but it is when hydrochloric acid is added. All the soluble salts of manganese investigated accelerate and increase liver autolysis; the carbonate inhibits it by preventing acid formation. A low concentration of hydrochloric acid accelerates autolysis, probably by so altering the proteins as to render them available substrates. The same is true for low H-ion concentrations generally. Edestin is sensitive to low acidity; egg-albumin requires more. Atrophy and necrosis of the liver *in vivo* is believed to be autolysis accelerated by production of acids. W. D. H.

The Supposed Synthesis of Uric Acid from its Decomposition Products by Tissue Extracts. Henry Michael Spiers (*Biochem. J.*, 1915, **9**, 337—341).—Ascoli and Izar's experiments were repeated, but no uric acid was formed from its decomposition products, or from dialuric acid and urea, under the influence of ox-liver extracts under anaërobic conditions. W. D. H.

The Rôle of Halogens as Accelerators of Tissue Enzyme Action. MAX MORSE (*J. Biol. Chem.*, 1915, **22**, 125—132).—Iodine and its inorganic compounds only slightly modify the rate of autolysis, probably by the formation of small amounts of hydrogen iodide. Organically bound iodine (such as thyroiodine) apparently accelerates it, but this is doubtless due to the extra substrate added. Bromine in minute amounts accelerates, owing to increase in H ion concentration. The feeding of dogs with thyroid for two weeks does not increase liver autolysis subsequently.

W. D. H.

The Influence of the Vagus on the Gaseous Metabolism of the Kidney. ROY G. PEARCE and EDWARD P. CARTER (*Amer. J. Physiol.*, 1915, **38**, 350—355).—The oxygen consumption of the kidney is unaffected by stimulation of the vagus or section of the splanchnic nerve. This is against the existence of renal secretory fibres. W. D. H.

The Selective Activity of the Human Kidney OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1915, **22**, 321—326).—The urine should be regarded as a mixture of different and more or less independent excretions, and thus specific functional deteriorations, such as "salt retention" and "nitrogen retention," may occur in disease. The present cases had been operated on for bladder disease, and so it was possible to collect the urine from each kidney separately. In all four cases back pressure had produced some hydronephrosis, a condition believed to injure convoluted tubules rather than glomeruli. The analytical results are not very uniform, but, so far as they go, they show that salt excretion was less affected than nitrogen excretion. W. D. H.

Does Fat Formation Occur in the Perfused Kidney? FRANK P. UNDERHILL and BYRON M. HENDRIX (*J. Biol. Chem.*, 1915, **22**, 471—475).—Gross and Vospahl state that perfusion of a rabbit's kidney with warm Ringer's solution for twenty-four hours leads to a percentage or absolute increase in the fat of the cortex; this is confirmed, but the interpretation is not a formation of fat from protein, but that the increase is due to a mechanical difficulty in preventing contamination with fat of the portion of material to be analysed. Mere suspension of the kidney in the solution leads to similar results. W. D. H.

The Action of Aseptic Tissue on Glucosone. P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1915, **22**, 337—339). - In animal oxidation, hexose is transformed into lactic acid, two molecules of methylglyoxal being intermediate. If, however, one hydrogen atom of the hexose is replaced by an organic or mineral radicle, the sugar is not affected by the tissue enzyme. In the present work, glucosone was investigated; theoretically, it might dissociate into glyceraldehyde and hydroxymethylglyoxal, and these in turn might be changed into lactic and pyruvic acids respectively; on

the other hand, glucosone may be regarded as a substituted glyoxal, and might be expected to be transformed into a hexonic acid. In the experiments recorded with aseptic kidney tissue, the glucosone solutions remained unchanged. It is only unchanged hexose which the enzyme can affect. W. D. H.

The Silicic Acid Content of Human Pancreas and the Weights of these Glands in Individuals of Different Ages. HUGO SCHULZ (*Biochem. Zeitsch.*, 1915, **70**, 464—488).—The silicic acid content of the pancreas from seventy-five cases of various diseases was estimated. No correlation between the disease and the amount of silica in the pancreas could be detected, and the author was unable to confirm Kahle's statements that this substance is less than normal in tuberculous and more than normal in cancerous individuals. The author tabulates the average amounts of silica in the pancreas of individuals of different ages, and also the weights of these glands. S. B. S.

Changes of Iodine Content of the Thyroid Gland following Changes in the Blood-flow. C. F. WATTS (*Amer. J. Physiol.*, 1915, **38**, 356—368).—The thyroid is the most vascular organ of the body, and even transient disturbances of the blood-supply induce marked changes in thyroid activity (discharge of iodine, etc.), both in health and disease. Stimulation of its vaso-constrictor nerves, or a decrease in its blood-supply, produced mechanically, causes a decrease in its iodine and water content. No histological changes are seen. The difficulty of deciding whether vaso-motor effects or the activity of secretory nerves is being dealt with is noticeable in many investigations, for instance, in those on the adrenals, but the balance of evidence appears to be against the existence of secretory nerves in the thyroid. W. D. H.

The Presence of Iodine in Tuberculous Tissues and in the Thyroid Gland. PAUL A. LEWIS and ROBERT B. KRAUSS (*J. Biol. Chem.*, 1915, **22**, 159—163).—Iodine is frequently present in tuberculous tissues, even if no iodine is administered. The main observations recorded are on rabbits and guinea-pigs. This result lessens the force of the conclusion that tubercular deposits have a special affinity for iodine when given as a drug. The nature of the iodine compounds present is not yet known, but its amount is quite independent of that in the thyroid; indeed, in rabbits, iodine may be absent from the thyroid altogether. Krauss' palladous iodide method (this vol., ii, 791) was used. W. D. H.

Absorption in Vivo of Iodine by Dogs' Thyroid Glands. DAVID MARINE (*J. Biol. Chem.*, 1915, **22**, 547—550).—The experiments emphasise the great affinity of thyroid tissue for iodine. As much as 18·5% of a given intake of iodine by the mouth may be recovered from a thyroid the ratio of which to the body-weight is 1:687. Maximum thyroid effects are induced by minimum amounts of iodine. The amount of a given intake absorbed de-

pends, for the most part, on the size of the gland and the existing degree of hyperplasia, or the degree of saturation with iodine at the time of the administration. W. D. H.

The Effect of Pituitary Substance on the Egg-production of the Domestic Fowl. Lewis Neilson Clark (*J. Biol. Chem.*, 1915, **22**, 485—491).—Feeding with anterior lobe of the pituitary gland increases the egg-production of hens whose production-curve is on the decline. It is effective after the fourth day of feeding, and persists several days after the last dose. The hatchability of the eggs is also increased. W. D. H.

The Influence of Extract of the Posterior Lobe of the Pituitary on the Secretion of Saliva. G. O. Solem and P. A. Lommen (*Amer. J. Physiol.*, 1915, **38**, 339—349).—Injection of pituitrin causes a decrease in the flow of the submaxillary secretion (dog and cat). This is partly due to inhibition of secretory nerve fibres, and after the injection pilocarpine is relatively ineffective; it is also in part due to diminished blood-supply, owing to vaso-constriction. W. D. H.

Estimation of Total Protein and Non-protein Substances in Muscle. N. W. Janney and F. A. Csonka (*J. Biol. Chem.*, 1915, **22**, 195—201).—The non-protein substances in muscle can be removed by successive extraction with hot (90°) acid salt solution, alcohol, and ether. In various animals the amount of protein in the fresh tissue varies from 15·4 to 17·8%, and the general composition of muscle protein is nearly the same for all species of the higher animals. The amount of non-protein substances is more variable, but the number of analyses is regarded as too small for the drawing of averages. W. D. H.

The Origin of Creatine. L. Baumann and J. Marker (*J. Biol. Chem.*, 1915, **22**, 49—53).—The muscles of a dog's hind limb were perfused with certain possible precursors of creatine, but neither arginine nor methylcarbamidoacetic acid gave rise to any appreciable increase in muscle creatine. W. D. H.

Extractive Substances of Muscular Tissue. XVII. One of the Causes of the Deficit on Determination of the Distribution of Nitrogen. I. A. Smorodincev (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1272—1274).—Investigation of the quantitative distribution of nitrogen in the different fractions obtained by Gulevitsch's method from the extracts of animal organs shows that a loss of nitrogenous substances occurs on precipitation by the different reagents (compare Skvorcov, A., 1910, ii, 879). One of the causes of this loss is found to be the absorption (? adsorption) of free hypoxanthine by barium sulphate. T. H. P.

Extractive Substances of Muscular Tissue. XVIII. Double Compound of Creatinine with Silver Nitrate. I. A. Smorodincev (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1275—1279).—From the flesh of the pig or ox, but not from that of the sheep, the

author has obtained the double compound of creatinine and silver nitrate, $C_4H_7ON_3,AgNO_3$, previously obtained by Neubauer (*Annalen*, 1861, **119**, 45). It is found that, under the influence of silver nitrate in a slightly acid medium, creatine undergoes transformation into creatinine, and it seems probable that the gelatinous precipitate obtained consists at first of the silver derivative of creatine. T. H. P.

The Ash of Clam Muscle in Relation to its Osmotic Properties. EDWARD B. MEIGS (*J. Biol. Chem.*, 1915, **22**, 493—498).—The figures for potassium, phosphorus, and total sulphur are very close to those obtained in frogs and mammals, but the sodium and chlorine are higher, but low in comparison with sea-water. The ash is not sufficient to bring the osmotic pressure up to that of sea-water; it follows that a large proportion of the water of the clam's muscle is combined with colloids, so that it cannot act as a solvent for salts. Some experiments are described which throw light on the manner in which the elements of the ash are combined in the living tissue; it is shown, for instance, that at least 88% of the sodium and chlorine are present as sodium chloride, and that not more than half of the potassium, is combined with phosphorus as potassium phosphate. Details are also given in regard to the partition of sulphur. Clam's muscle remains highly irritable after being forty hours or more in 30% solution of sucrose. W. D. H.

The Osmotic Properties of Calcium and Magnesium Phosphate in Relation to those of Living Cells. EDWARD B. MEIGS (*Amer. J. Physiol.*, 1915, **38**, 456—489).—Semi-permeable membranes can be formed from both calcium and magnesium phosphates. The former is nearly impermeable to sucrose, dipotassium phosphate, and calcium chloride, slightly permeable to sodium chloride, and quite permeable to potassium hydroxide. The latter is impermeable to sucrose, dipotassium phosphate, and magnesium chloride, somewhat permeable to sodium and potassium chlorides, and highly so to ethyl alcohol. Some anomalous results are described which obtain when these membranes, and also copper ferrocyanide membranes, are subjected to the action of neutral electrolytes and alkalis. The semi-permeable properties of celloidin membranes depend on their physical state, and this is probably true for such membranes in general. Evidence is adduced that these membranes are always colloidal, and that the passage of water through them is the result of unequal hydration of the colloid at the two surfaces. W. D. H.

Composition of Brachiopod Shells. F. W. CLARKE and W. C. WHEELER (*Proc. Nat. Acad. Sci.*, 1915, **1**, 262—266).—A number of analyses of the shells of brachiopods have been made. The analytical results, which in general confirm previous analyses, show that brachiopods are to be divided into two groups: (1) those with shells containing large amounts of calcium carbonate and little

phosphates and organic matter, and (2) those containing large amounts of calcium phosphate and organic matter with small amounts of carbonates. Of the first group, specimens of *Terebratula cubensis* (coast of Florida), *Terebratulina septentrionalis* (Eastport, Maine), *Laqueus californicus* (Esteros Bay, California), *Rhynchonella psittacea* (Shetlands), and *Crania anomala* (coast of Norway) have been analysed, and found to contain 98·61—88·59% of calcium carbonate, ignoring the organic matter, which was present in the quantity 4·73—0·93%. Of the second group, specimens of *Lingula anatina* (coast of Higo Province, Japan, and also Iloilo, Philippine Islands), *Discinisca lamellosa* (coast of Peru), and *Glottidia pyramidata* (coast of North Carolina) have been analysed, and these contained 91·74—74·73% of calcium phosphate, the organic matter being ignored. The amount of organic matter varied between 40 and 25%. J. F. S.

The Coefficient of Osmotic Pressure of Bombyx novi, L. During the Whole Period of its Development. Osw. Polimanti (*Biochem. Zeitsch.*, 1915, **70**, 74—92).—The depression of the freezing point of the paste obtained from the powdered insects or (in the case of large larvæ) of the blood was measured in all the stages of the development from the egg to the complete insect. The variation of Δ from 0·690 to 1·364 was found in different stages, the biological significances of which are discussed by the author. S. B. S.

The Rate of Passage of Fatty Acid of Food into the Mammary Glands of the Goat. O. C. Bowes (*J. Biol. Chem.*, 1915, **22**, 11—13).—Arachidic acid given as food appeared in the milk of a goat twelve and a-half hours later. W. D. H.

The Action of Pituitrin on Milk Secretion. A. L. I. Maxwell and A. C. H. Rothera (*J. Physiol.*, 1915, **49**, 483—491).—Pituitrin causes a gradual rise of milk pressure, which is maintained for seventeen minutes in goats and forty minutes in cows. In the goat, however, extra milk is available for a longer time. If the effects were due to muscular contraction, this continuance would not be explicable. In cats, about 60% of the milk is preformed in the gland after six to seven hours' interval, and about 40% is secreted during suckling, that is, suckling causes a true secretion. Pituitrin is also concluded to produce a true secretion. W. D. H.

The Secretion of Bile. Seizaburo Okada (*J. Physiol.*, 1915, **49**, 457—482).—Diets of bread, butter, and meat of equal caloric value cause little difference in the secretion of bile. The secretion lessens sooner after bread than after meat or butter. Inanition lessens the secretion and the excitatory effects of food. The secretion increases when the following substances are introduced into the stomach: raw or boiled egg-white, fat, oil, soap, acids (very marked), commercial peptone, Liebig's extract, bile salts, and bile.

In the case of bile and bile salts, the bile secreted, although pale in colour, contains more solids. Dilute bile is formed when secretin is injected into the blood stream; Witte's peptone has a similar effect; injection of hæmoglobin increases the bile pigment. The following substances introduced into the stomach have little or no effect: sucrose, cakes of baked starch or sugar, water, sodium hydrogen carbonate; the following drugs increase the bile-flow: sodium salicylate, salol, chloral hydrate, cream of tartar, and alcohol in large doses. Calomel has no effect. Atropine causes a slight diminution, pilocarpine a slight increase, and nicotine an inconstant increase of secretion. W. D. H.

Diuresis: the Pituitary Factor. Douglas Cow (*J. Physiol.*, 1915, **49**, 441—451).—The diuresis which follows injection of extracts of duodenal mucous membrane is independent of their salt contents, although such salt content may also increase the flow of urine; it is mainly dependent on the activity of the pituitary gland, which is stimulated by these extracts. Diuresis produced by increased fluid probably depends on absorption from the intestine, which carries with it the substance from the duodenum which stimulates the pituitary. W. D. H.

The Mineral Excretion of the Monkey. L. Baumann and E. Oviatt (*J. Biol. Chem.*, 1915, **22**, 43—45).—Observations on a Macaque monkey on a constant diet of bananas and milk showed that it retained 3·5% of the ingested nitrogen. The average ammonia nitrogen in the urine was 1·4% of the total; the sulphur as sulphate, ethereal sulphate, and unoxidised sulphur was 60·9, 16·9, and 22·2% respectively; the corresponding figures in man are 87·8, 6·8, and 5·1%. The chlorine was almost entirely excreted by the kidneys, but 98% of the phosphorus, 80% of the calcium and magnesium, and 25% of the sodium and potassium were found in the fæces. W. D. H.

The Excretion of Free and Conjugated Phenols and Phenol Derivatives. Otto Folin and W. Denis (*J. Biol. Chem.*, 1915, **22**, 309—320).—The excretion of total phenol products in the urine is greater than indicated in previous work. They are not wholly converted into conjugated phenols. The detoxication involved in such conjugations is therefore only partial. The total excretion tends to vary directly, but not proportionally, with the protein intake. W. D. H.

The Rôle of the Digestive Glands in the Excretion of Endogenous Uric Acid. Lafayette B. Mendel and Raymond L. Stehle (*J. Biol. Chem.*, 1915, **22**, 215—230).—The data presented support the view that part of the endogenous uric acid originates from the activity of the digestive glands. It is increased by pilocarpine, which stimulates these glands, and by protein food, the most important succagogue. It is lessened by atropine, which inhibits secretion. Indigestible material (agar-agar) causes no

effect, so muscular action is unimportant in the production of uric acid. The conclusions of Raiziss, Dubin, and Ringer (this vol., i, 70, 744) are criticised. W. D. H.

The Nitrogen Excretion of the Cat During a Purine-free and a Purine-rich Diet. FREDERICK S. HAMMETT (*J. Biol. Chem.*, 1915, **22**, 551—558).—With the exception of uric acid, the excretion by the cat of nitrogenous urinary constituents is governed by the same laws as in man; hence the usefulness of this animal for general metabolic work. In reference to purine metabolism, the case is different. On a purine-free diet, the amount of uric acid excreted is insignificant. On a purine-rich diet, the increase denotes an overburdening of the uricolytic enzymes.

W. D. H.

The Relation between the Administration of Tryptophan to Dogs, and the Elimination of Kynurenic Acid in their Urine. ANNIE HOMER (*J. Biol. Chem.*, 1915, **22**, 391—405).—Kynurenic acid is not readily capable of further utilisation in the body of the dog. All that is given is excreted in the urine. The production of kynurenic acid from tryptophan does not represent either the only or the main line of the breakdown of tryptophan, especially in young dogs. A certain amount of the tryptophan is "side-tracked" into kynurenic acid, but the remainder is utilised in some direction not yet elucidated. W. D. H.

The Diazo-reaction of Dog's Urine and its Relationship to Metabolic Processes. M. MASSLOV (*Biochem. Zeitsch.*, 1915, **70**, 306—316).—The relative amounts of the chromogen (the substances giving a colour reaction with diazo-compounds) found in the normal urine of dogs were estimated colorimetrically by the process employed by Weiss and Sobolev for the estimation of histidine (A., 1914, ii, 155). The amount of "diazochromogen" excreted was found to be independent of the amounts of histidine complexes (including carnosine) that were ingested, but ran more or less parallel with the nitrogen in the urine. The chromogen appears, however, to be derived more from the breakdown of the tissues than from ingested proteins, and to be, therefore, to a large extent of endogenous origin. The results support the supposition of Weiss that diazochromogens belong to the group of the oxyproteic acids. S. B. S.

A Spectroscopic Examination of the Colour Reactions of Certain Indole Derivatives and of the Urine of Dogs after their Administration. ANNIE HOMER (*J. Biol. Chem.*, 1915, **22**, 345—368).—The materials used were identified by their absorption spectra. Indole, scatole, indolealdehyde, indolecarboxylic acid, and indoleacetic acid undergo but little change in their passage through the animal body; in indolepropionic acid, more deep-seated changes take place. Tryptophan is not normally broken down into any of these substances before absorption from

the alimentary canal. The urorosein reaction of urine is due to indoleaceturic acid, produced by bacterial action in the intestine from tryptophan via indoleacetic acid. Under some conditions this reaction is changed to that of indoleacetic acid. Scatole-red has the same absorption spectrum as urorosein, but the two are really different. Scatole-red is a mixture of two pigments which can be separated by suitable solvents; the stability and solubility of the mixture are different from those of urorosein. The indican reaction is given by dog's urine within a short time after the administration of indole and indolealdehyde, and persists for some days, but it does not appear until the second day after scatole is given. Indoxyl compounds in human urine may arise when the liver cannot deal with tryptophan beyond the indolealdehyde stage, or by the absorption of indole or its aldehyde produced by the intestinal putrefaction of tryptophan. W. D. H.

Variations in the "Leak-point" in Diabetes. I. Low Level. GEORGE GRAHAM (*Proc. physiol. Soc.*, 1915, xlvi—xlvii; *J. Physiol.*, **49**).—A case is recorded in which sugar appeared in the urine even although the blood-sugar was but little increased. Hourly estimations of blood-sugar and urinary-sugar were made before and after meals. Control observations on a healthy man showed a slight rise in blood-sugar after a meal, but no glycosuria; in the diabetic person there was a similar rise in the sugar during the first two hours after the meal, but glycosuria resulted. As in cases of the kind previously reported by others, but without details, the kidney is regarded as at fault, so that it allows the easy escape of sugar. W. D. H.

Variations in the "Leak-point" in Diabetes. II. High Level. GEORGE GRAHAM (*Proc. physiol. Soc.*, 1915, xlviii—xlix; *J. Physiol.*, **49**).—Sugar usually passes into the urine when its amount in the blood rises more than 0·18—0·2%, but hyperglycæmia in fevers and nephritis has been recorded without glycosuria; 0·28 is the highest figure recorded in fevers. A raising of the "leak point" may, however, occur in diabetes itself, causing cessation, more or less temporary, of the excretion of sugar in spite of carbohydrate in the diet. In one of the two cases given to illustrate this, the blood-sugar rose to more than 0·25% without glycosuria. W. D. H.

Narcosis. III. Narcosis and Asphyxiation. HANS WINTERSTEIN (*Biochem. Zeitsch.*, 1915, **70**, 130—143).—As the result of experiments on the spinal chord of frogs, the author draws the following conclusions: The diminution of the oxidation processes in narcosis is a secondary phenomenon, and does not explain the mechanism of narcosis. Narcosis does not inhibit the accumulation of acid products which takes place in absence of oxygen, neither does it interfere with their removal when oxygen is supplied. Narcosis is not an asphyxiation, neither does it by prolongation lead to this state. It does not prevent the asphyxiation which

follows normally on deprivation of oxygen, although it retards recovery when oxygen is again supplied. S. B. S.

The Hexone Bases of Malignant Tumours. R. A. KOCHER (*J. Biol. Chem.*, 1915, **22**, 295—303).—In five cases of malignant tumour, the quantity of hexone bases was about double that found in normal tissue. W. D. H.

Effect of Intravenous Injections of Sodium Phosphates. ISIDOR GREENWALD (*J. Pharmacol. expt. Ther.*, 1915, **7**, 57—61).—Starkenstein (*Arch. expt. Path. Pharm.*, 1914, **77**, 45) states that injections of various sodium phosphates cause twitchings, tremors, and convulsions, and explains this result as due to precipitation of calcium ions; this is counteracted by giving calcium salts. This is of interest, since the tetany produced by removal of the parathyroids is attributed by some observers to paucity of calcium. Accordingly, Starkenstein's experiments were repeated on dogs and rabbits, but the results obtained were wholly negative. Gardner and Symes (A., 1911, ii, 314) obtained similar negative results on cats. W. D. H.

Carbohydrate Metabolism. X. The Influence of Hydrazine on the Respiratory Quotient and Heat Production. FRANK P. UNDERHILL and JOHN R. MURLIN (*J. Biol. Chem.*, 1915, **22**, 499—504).—The subcutaneous injection of hydrazine into fasting dogs increases the rate of carbohydrate combustion as measured by the respiratory quotient; this probably explains the fall in blood-sugar, and the disappearance of glycogen from the liver and muscles previously reported. Subcutaneously introduced, dextrose is oxidised more rapidly in dogs dosed with hydrazine than in normal fasting dogs. Such injections of sugar also appear to exert a "specific dynamic action." Hydrazine has no specific effect on heat-production. W. D. H.

The Differential Effects of Adrenaline on Splanchnic and Peripheral Arteries. FRANK A. HARTMAN (*Amer. J. Physiol.*, 1915, **38**, 438—455).—In a majority of animals, dilute adrenaline causes a fall in general blood-pressure. Large doses of ergotoxine inhibit the splanchnic response to adrenaline. The existence of vasodilator nerves in the peripheral arteries and their absence in the splanchnics is considered to be the explanation of the opposite action of adrenaline on the two sets of blood-vessels. W. D. H.

Physiological Action of Some Protein Derivatives. I. Are Proteoses Prepared from Zein and Gliadin Physiologically Active? FRANK P. UNDERHILL and BYRON M. HENDRIX (*J. Biol. Chem.*, 1915, **22**, 443—452).—The intravenous injection of zeoses (0·5 gram per kilo.) lowers arterial pressure and inhibits blood-coagulation. Smaller doses have no marked effect. Gliadoses lower the pressure less, but inhibit coagulation more strongly. W. D. H

Physiological Action of Some Protein Derivatives. II. The Relation of Racemisation to the Physiological Action of Proteins and Proteoses. FRANK P. UNDERHILL and BYRON M. HENDRIX (*J. Biol. Chem.*, 1915, **22**, 453–464).—Crude racemised proteins are toxic when introduced into the circulation; the effect of racemised zein is inconstant. Purified racemised proteins have no poisonous action, but the washings of the crude material have. Alcohol removes a part of the active substance from the crude racemised proteins. Proteoses obtained by acid digestion are probably as toxic as those from native proteins; caseoses and albumoses are quite toxic, but zeoses are inert. W. D. H.

Physiological Action of Some Protein Derivatives. III. The Physiological Action of Vaughan's "Crude Soluble Poison." FRANK P. UNDERHILL and BYRON M. HENDRIX (*J. Biol. Chem.*, 1915, **22**, 465—470).—Vaughan's poison is prepared by digesting any true protein with alcoholic sodium hydroxide. It is more toxic than Witte's peptone, and restrains blood-clotting (contrary to Edmund's statement). Its general action is similar to that of proteoses, and small doses produce in rabbits marked symptoms, and even death. Boiling with dilute hydrochloric acid to the abiuretic stage destroys its toxicity. W. D. H.

Peptone Hypoglycæmia. HUGH MCGUIGAN and ELLISON L. ROSS (*J. Biol. Chem.*, 1915, **22**, 417—423).—The intravenous injection of proteose and peptone in most cases causes pronounced hypoglycæmia. This seems to be due to circulatory changes in the liver. W. D. H.

The Formation of Specific Proteolytic Enzymes in Response to the Parenteral Introduction of Foreign Protein. ALONZO E. TAYLOR and FLORENCE HULTON (*J. Biol. Chem.*, 1915, **22**, 59–61).—Protamine from the salmon was introduced into the circulation of rabbits. No protective enzyme could be subsequently found in the blood. W. D. H.

Comparative Investigations on the Toxicity of Arsenious and Arsenic Acids. GEORG JOACHIMOGLU (*Biochem. Zeitsch.*, 1915, **70**, 144—157).—The relative toxicity of arsenious and arsenic acids, as measured by the intravenous injection of the sodium salts into rabbits, is in the ratio of about 6 : 10. Arsenious acid is, however, about 300 times as toxic as arsenic acid when acting on the isolated frog's heart. It is also very much more toxic to the isolated small intestine of a rabbit, although the differences between the acids are not so marked as is the case with the frog's heart. Apparently the arsenic acid only acts toxically after reduction to arsenious acid. S. B. S.

The Inactivation of Serum by Cobra Poison. L. HIRSCHFELD and R. KLINGER (*Biochem. Zeitsch.*, 1915, **70**, 398—415).—The hæmolytic action of cobra poison is not materially affected by

heating, neither is its destructive action on cytozymes. On the other hand, heat has a considerable effect on that constituent of the poison which antagonises the action of the complement. This component is also very sensitive to the action of acids, and loses its action when the poison is kept in contact for only a short time with very dilute hydrochloric acid. From these results, the conclusion is drawn that the lipolytic- and complement-destroying functions of cobra venom are due to different mechanisms. It is also shown that in the presence of citrates and hypertonic solutions the complement is not appreciably weakened, even by prolonged contact with the cobra venom. From these and other experiments the conclusion is drawn that the change produced in serum by the cobra poison is due, not to a destruction of a definite substance (for example, through lipase action), but to change produced in the state of the globulins, such as can be effected by certain treatments which produce precipitation, such as dilution with water, or addition of various suspensions, or by shaking. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Azotobacter and Nitrogen Fixation in Indian Soils. J. H. Walton (*Mem. Dept. Agric. India Bact. Ser.*, 1915, **1**, 97—112).—The nitrogen-fixing power of *Azotobacter* in cultures inoculated with Pusa soil compares favourably with that observed elsewhere. The pure cultures obtained from different soils were found to vary both in nitrogen-fixing powers and in their morphological and cultural characters. Black pigment was only produced in impure cultures.

The results of inoculation experiments, made nearly every week for a year, showed that fixation of nitrogen is lowest from October to January, and highest from June to September, the low results being coincident with the drying of the soil and lowering of the temperature, and the high results with a fairly high temperature and the rainy season. N. H. J. M.

Process of Denitrification in Arable Soil. C. Lumia (*Ann. Chim. applic.*, 1915, **4**, 1—55).—Experiments on the effect of limited aeration, the action of some manurial substances, the effect of the amount of nitrate present, the action of fresh and mature farmyard manure, cereal straw and green leguminous plants, and the influence of soil moisture and temperature on denitrification.

Under the conditions of the experiments, the effect of confined air as compared with no air was to reduce the period of incubation; in a given time, however, the amount of nitrate decomposed was less with air than under absolutely anaerobic conditions.

Basic slag quickened the process of denitrification, but after about a week the amount of nitrogen was somewhat less than in the control experiment. Ammonium sulphate had no effect, whilst calcium cyanamide (0·25—0·15%) retarded denitrification.

When the amount of potassium nitrate varied from 0·5 to 25 per thousand, denitrification was more active with the lower than with the higher amounts, and the maximum period of incubation was with the highest amount of nitrate.

A number of other experiments are described in which the rate of denitrification in presence of various substances was ascertained. In presence of citric acid, addition of straw was without effect. Addition of citric acid to the nutritive solution nearly doubled the amount of nitrogen produced in fifteen days as compared with the same solution without citric acid. Fresh and mature dung gave about the same results; straw was more favourable to denitrification, whilst still higher results were obtained with green bean-stalks. N. H. J. M.

The Action of the Ferments of Carbamide in the Destruction of Organic Matter. F. Bordas and S. Bruère (*Compt. rend.*, 1915, **161**, 285—287).—A comparison of the rate of destruction of fœtal organic matter immersed in culture liquids containing, respectively, the ferments of carbamide, intestinal bacilli, micro-organisms of cellulose fermentation, and a mixture of all three, shows that the dissolving action of the carbamide ferments was much more energetic than that of the others. If, however, the fœtus of a pig was submitted to the action of these carbamide ferments, under perfectly aseptic conditions no decomposition was noticeable, even after twenty days. The general experimental results show that, given moisture and a suitable temperature, the ferments which decompose carbamide are the most satisfactory in producing a rapid destruction of organic matter. W. G.

The Final Hydrogen Ion Concentrations of Cultures of Bacillus coli. W. Mansfield Clark (*J. Biol. Chem.*, 1915, **22**, 87—98).—Several cultures of the organism were used to ferment dextrose and lactose, and the final H-ion concentration was determined electrometrically. In any given medium the values agree well, but with different media they vary, the greater the buffer effect of the medium the higher being the concentration. This suggests the accumulation of other toxic substances, each of which produces a small effect. The final concentrations differ so little that the claim of Michaelis and Marcora that we have to deal with a physiological constant is supported. W. D. H.

The Reducing Enzyme of Bacillus coli communis. Arthur Harden and Sylvester Solomon Zilva (*Biochem. J.*, 1915, **9**, 379—384).—*B. coli*, when washed, does not reduce methylene-blue, but does so on the addition of certain reagents, which vary widely in chemical nature. The effect of adding broth and glycerol, respectively, show there are two factors, one which activates, the

other which retards, the reduction. The time of reduction decreases with increase of emulsin, and increases with the amount of methylene-blue if the emulsin is the constant. W. D. H.

The Inhibition of Indole Formation by B. coli in Culture Media to which Sugars have been Added. ALBERT FISCHER (*Biochem. Zeitsch.*, 1915, **70**, 105—118).—The sugars investigated were lactose, maltose, galactose, lævulose, and dextrose, and of these only the last-named completely inhibited the formation of indole. The inhibition was complete after forty-three hours with concentrations between 1·80 and 2·25% . The acid which is formed plays no part in this inhibition, so that neither the hydrion concentration nor the concentration of the undissociated acid plays any part in the action. The dextrose appears to have the property of inactivating the proteolytic ferment of the bacterium. The differences in the concentration of the peptone used in the culture media had no influence on the indole formation. S. B. S.

The Stimulating Action of Magnesium Salts on Lactic Fermentation. CHARLES RICHET (*Compt. rend.*, 1915, **161**, 264—265. Compare A., 1893, ii, 179).—The optimum amount of magnesium chloride, $MgCl_2,6H_2O$, in increasing the production of lactic acid during fermentation is about 12·5 grams per litre, this being also about the optimum amount found for this salt in phagocytosis by Delbet (compare *Compt. rend.*, 1915, **161**, 268). W. G.

The Action of Certain Lactic Acid Bacteria on Proteins and Other Nitrogenous Compounds. A. STUTZER (*Biochem. Zeitsch.*, 1915, **70**, 299—305).—Experiments were made with *B. Delbrückii* (warm lactic acid bacillus) and *B. cucumeris fermentati* (cold lactic acid bacillus), which are used in the preparation of ensilage, to ascertain their action on proteins and other nitrogenous substances. It was found that both kinds rapidly produced acid, but did not break down proteins into amino-acids. When allowed to grow on media containing other nitrogenous substances, the *B. cucumeris fermentati* converted only 1·8% of ammonium acetate, 17·4% of asparagine, and 6·5% of carbamide into proteins under the conditions of experiment employed. There is no evidence, therefore, that the proteins of fodder can be increased by the addition of simpler nitrogenous compounds to the materials employed for ensilage. S. B. S.

The Fermentation of Pyruvic Acid by Bacteria. II. L. KARCZAG and L. MÓCZÁR (*Biochem. Zeitsch.*, 1915, **70**, 317—319. Compare A., 1913, i, 1280).—The experiments confirm the specific biological relationship between pyruvic acid and dextrose, discovered by Neuberg and Karczag, according to which only those bacteria which produce fermentation of the sugar act on the acid. The following bacteria, which act on sugar, were found to decompose the acid: *B. typhi murium*, *B. pneumoniae Friedländer*, and *B. oedematis maligni*. S. B. S.

The Fermentation of Pyruvic Acid by Bacteria. III. L. KARCZAG and ELSE BREUER (*Biochem. Zeitsch.*, 1915, **70**, 320—). —In contrast to yeast and various saprophytic bacteria of putrefaction, which decompose α-keto-acids as well as acids of most varied description with evolution of gas, certain pathogenic bacteria which ferment pyruvic acid are almost without action on the higher members of the class of α-keto-acids. S. B. S.

The Fermentation of Pyruvic Acid by Bacteria. IV. L. KARCZAG and E. SCHIFF (*Biochem. Zeitsch.*, 1915, **70**, 325—332).—Pyruvic acid is decomposed almost quantitatively into gaseous products by *B. coli*, with the formation of a number of intermediate products. The gases formed consist of about 90% hydrogen and 19% carbon dioxide. Formic and acetic acids could not be detected as intermediate products, and the increase of butyric and propionic acids is attributed to secondary processes. Formic and glycollic acids are acted on, with evolution of hydrogen, by a number of bacteria which ferment pyruvic acid, including *B. coli*, *B. paratyphi*, *B. enteritidis Gaertner*, *B. typhi murium*, and *B. pneumoniae*. These results justify the assumption of a specific biological relationship between pyruvic acid on the one hand, and formic and glycollic acids on the other. The latter may be regarded as intermediary products in the pyruvic acid fermentation. S. B. S.

The Yoghurt Bacillus. F. DUCHÁČEK (*Biochem. Zeitsch.*, 1915, **70**, 269—293).—Investigations have been carried out to explain the differences in the action of the milk-souring bacillus as described by Effront on the one hand, and by Bertrand, the author, and others on the other. According to the former, the bacillus exerts a strong proteoclastic activity on caseinogen, a reaction which was found to be wanting by other investigators. A comparison was therefore made of the action of strains of bacilli obtained from Effront (from a commercial medicinal source) and from Metschnikov, which was recognised as a true strain of *B. bulgaricus*. The investigations revealed many marked differences. The latter strain is much more sensitive, is readily killed by acids, and will only develop in certain culture media, which must contain sugars. The bacillus obtained from Effront was much less sensitive, and, in contrast to the true *B. bulgaricus*, readily digested proteins. Other marked differences were found, and reasons are given for supposing that Effront's bacillus was not a mere biological modification of the true Yoghurt bacillus. Attention is directed to the difficulty of completely sterilising milk, to the ease with which the true *B. bulgaricus* is destroyed, and to the great possibilities of this taking place in commercial preparations, and the predominance in these of other strains of bacteria which remain owing to incomplete sterilisation. S. B. S.

The Comparative Rate at which Fluorescent and Non-fluorescent Bacteria are Killed by Exposure to Ultra-violet Light. W. E. BURGE and A. J. NEILL (*Amer. J. Physiol.*, 1915, **88**, 401—405).—Fluorescent bacteria are relatively highly resistant

to the deleterious action of ultra-violet rays. Like the lens protein, they are able to protect themselves from the coagulative effect of these rays by being able to convert rays of short wave-length into longer waves, and thus dispose of the energy of the absorbed short waves. This power is absent in non-fluorescent bacteria.

W. D. H.

The Influence of the Alternating Current on the Fermentation of Living Yeast. ERIK HÄGGLUND (*Biochem. Zeitsch.*, 1915, **70**, 164—170).—There is an increase in the zymase activity in living yeast when the culture is submitted to the action of an alternating current. This is most marked at the commencement of the fermentation, and may reach as much as 100%. After a time, however, the increase of the fermentation produced by the current diminishes, and when 20% of the sugar has been fermented, the rate is not larger than in the control experiments. The current does not lead to an increase in the hydrion concentration as compared with the increase in the control experiments. It is suggested that acids inhibit the acceleratory action of the alternating current.

S. B. S.

Carboxylase and Other Ferments of Yeast. CARL NEUBERG (*Biochem. Zeitsch.*, 1915, **71**, 1—103).—Experiments are quoted to illustrate the stability of the carboxylase in permanent preparations. The carboxylase is not destroyed when made from yeast-juice which has been heated for ten minutes at 54—55°; such a preparation was without fermentative action on sugar. The carboxylase also acts on pyruvic acid after the yeast-juice has been submitted to dialysis. Yeast in which the sugar-fermenting properties have been exhausted by fermentation retains the carboxylase which still exists in juices which have been kept for prolonged periods, and in which putrefaction even has started. The carboxylase action can take place between 10° and 20°. At such temperatures the action can be demonstrated, not only on pyruvic acid, but on other α-keto-acids, such as oxalacetic acid and methylethylpyruvic acid. The highest temperature of action is 70° for the carboxylase of fresh yeast; for maceration juices or permanent preparations the critical temperature is 65—68°. The corresponding temperatures for the zymase action are 70° and 51°.

The carboxylase reaction takes place best in the presence of a "buffer." That generally employed was dipotassium hydrogen phosphate, and borates are equally effective. The action of the "buffers" is illustrated by a large number of curves, showing the relative rates of reaction for the decomposition of pyruvic acid in the presence and absence of buffers, when both fresh yeasts and dried preparations were employed. The carboxylase action is readily destroyed by previous treatment of the yeast with acids or alkalis and subsequent neutralisation. The carboxylase is very insensitive to the action of various organic substances, such as the alcohols, glycols, glycerol, acetone, pyridine, and the aldehydes. The majority of the experiments dealing with this subject were carried out with maceration juice, to avoid osmotic effects.

The influence of buffers on the carboxylase action on the higher keto-acids (oxalacetic and α-ketobutyric acids) was investigated. In these cases, the buffers (potassium phosphate and arsenate) did not exert the favourable influence that was noticed in the case of pyruvic acid.

Carboxylase exists in plasmolysed yeast.

The presence of pyruvate (and the exertion of a carboxylase action) does not inhibit the invertase action of yeast; rather it causes, generally, a slight stimulation of this action. The general conclusion is drawn that the invertase action is independent of that of the carboxylase.

Experiments to determine whether carboxylase and zymase actions taking place simultaneously inhibit one another (that is, to determine whether the carboxylase is a part of the zymase complex) did not lead to results which warrant any definite conclusion.

By treatment of a yeast with 2% of pyruvic acid at 37° for forty-eight hours, it loses both its carboxylase and zymase functions; similar treatment with 2% of dextrose leaves the fermentative functions intact. This action of pyruvic acid does not take place in the presence of a "buffer."

Potassium pyruvate stimulates the fermentative activity of yeast-juice on various sugars, including dextrose, lævulose, mannose, and the disaccharides sucrose and maltose. A similar activating action was observed with the salts of other keto-acids, including α-ketobutyric, α-ketohexoic, hydroxypyruvic, oxalacetic, α-ketoglutaric, phenylglyoxylic, phenylpyruvic, and hydroxyphenylpyruvic acids. These are all derivatives of various amino-acids derived from proteins, and it is suggested that there is some natural relationship between the processes of alcoholic fermentation, fermentation in the absence of sugars, and protein metabolism.

Experiments were carried out to determine the minimal amounts of material necessary to produce a carboxylase action, and these were found to be very small.

The autofermentation of sixty-seven maceration juices was determined. In nearly all these cases, when the juices were prepared by the method described by the author, there was no autofermentation.

Attention is directed to the great stability of invertase solutions, one of which was kept by the author for 800 days without undergoing injury. S. B. S.

The Fermentation of Dihydroxymaleic Acid. Carl Neuberg and Erwin Schwenk (*Biochem. Zeitsch.*, 1915, **71**, 104—113).—Under the influence of living yeasts, as well as of dried preparations and maceration juices, dihydroxymaleic acid undergoes decomposition at 16—18° to yield carbon dioxide and glycollaldehyde. The rate of decomposition is considerably greater than that of the spontaneous change which takes place under similar conditions in the absence of yeasts. The aldehyde was isolated in the form of the hydrazone, which was mixed with some of the osazone of hydroxypyruvic acid. The latter can be

separated from the former by extraction with a dilute solution of sodium carbonate. An improvement of Fenton's method for the preparation of dihydroxymaleic acid is described. S. B. S.

Phytochemical Reductions. X. Reduction of Glycollaldehyde to Ethylene Glycol. CARL NEUBERG and ERWIN SCHWENK (*Biochem. Zeitsch.*, 1915, **71**, 114—117).—The glycol was obtained by adding the aldehyde to sugar–yeast fermentation mixture in a yield of about 30% of the theoretical quantity. It was isolated and identified by oxidation to glycollaldehyde, which was obtained in the form of its *p*-nitrophenylosazone. S. B. S.

The Behaviour of α-Keto-acids towards Micro-organisms. III. The Putrefaction of *dl*-Methylethylpyruvic Acid [α-Keto-β-methylvaleric Acid]. CARL NEUBERG and BRUNO REWALD (*Biochem. Zeitsch.*, 1915, **71**, 122—125).—It has been shown by Neuberg and Peterson (this vol., i, 356) that this acid undergoes asymmetric change in the presence of yeast–sugar fermentations, yielding as chief product a *d*-amyl alcohol. It was therefore of interest to ascertain whether it also undergoes asymmetric change as the result of putrefaction. The chief product formed by micro-organisms from the acid was found to be α-methylbutyric acid, the *d*-variety being obtained mixed with about 70% of the racemic acid. A small amount of another acid, which is probably a hexoic acid, was also obtained. S. B. S.

Changes in the Alcohol and Aldehyde Content of Yeast on Keeping and on Autolysis. CARL NEUBERG and ERWIN SCHWENK (*Biochem. Zeitsch.*, 1915, **71**, 126—132).—Perfectly fresh yeast does not contain acetaldehyde, but if kept, acetaldehyde is formed, which can be separated by washing the yeast with tap-water and centrifuging. If living yeast is kept in air-tight boxes at 5°—10°, a marked increase in both the acetaldehyde and ethyl alcohol content can be detected. By the autolysis of both fresh and dried yeast in water saturated with carbon dioxide, an increase of both acetaldehyde and alcohol could be detected. There was no quantitative relationship between the increased acetaldehyde or alcohol formed, the increase in the amount of the former being always considerably larger than that of the latter. S. B. S.

The Relationsbip of the Carboxylase to the Zymase. CARL NEUBERG (*Biochem. Zeitsch.*, 1915, **71**, 133—134).—The three species of *Pseudosaccharomyces* (*germanicus*, *javanicus*, *indicus*), which were found by Klöcker to have no fermentative action on sugars, were also found to be without action on pyruvic acid. This is not due to the action of some inhibitory substance, but to the absence of a carboxylase, as the addition of an ordinary yeast to the mixtures containing these organisms and the substrates rapidly produced evolution of gas. S. B. S.

The Co-ferment Action of the Salts of α-Keto-acids. CARL NEUBERG and ERWIN SCHWENK (*Biochem. Zeitsch.*, 1915, **71**, 135—143).—It was found that a mixture of salts of α-keto-acids in

presence of dipotassium hydrogen phosphate could activate yeasts or yeast preparations which had been freed from the co-enzyme. No single salt was found to bring about this result. A mixture of potassium or calcium salts of the following acids was employed: pyruvic, α-ketobutyric, α-keto*iso*valeric, α-ketohexoic, phenylglyoxalic, phenylpyruvic, *p*-hydroxyphenylpyruvic, hydroxypyruvic, oxalacetic, and α-ketoglutaric acids. These may be considered as derivatives of amino-acids, and attention is directed to the possible connexion indicated by the experiments between the protein and carbohydrate metabolism of yeast. The properties of the co-enzyme of yeast and of the keto-acids indicate, furthermore, that there is nothing improbable in the assumption that the co-enzyme is a mixture of such acids. The amount of activation produced, however, by such an artificial co-enzyme is less than that produced by a natural one prepared (by dialysis, by heat, etc.) from yeast.

S. B. S.

The Mechanism of the Natural Formation of Succinic Acid. I. Formation by the Fermentation of α-Ketoglutaric Acid. CARL NEUBERG and M. RINGER (*Biochem. Zeitsch.*, 1915, **71**, 226—236).—By the action of fresh yeast or yeast-juice, α-ketoglutaric acid can be converted into succinic acid, and a nearly theoretical yield has been obtained. This formation is in marked contrast to the formation of succinic acid from glutaric acid, which only takes place in the presence of living and fermenting yeast. S. B. S.

The Mechanism of the Natural Formation of Succinic Acid. II. The Formation of Succinic Acid by the Putrefaction of α-Ketoglutaric Acid. CARL NEUBERG and M. RINGER (*Biochem. Zeitsch.*, 1915, **71**, 237—244).—Succinic acid has been obtained by the putrefaction of α-ketoglutaric acid in yields varying between 14 and 19%. In addition, formic, acetic, and propionic acids are formed. S. B. S.

Phytochemical Reductions. XI. The Conversion of Ethyl Disulphide into Ethyl Mercaptan. CARL NEUBERG and ERWIN SCHWENK (*Biochem. Zeitsch.*, 1915, **71**, 118—121).—This reduction takes place according to the equation $Et{\cdot}S{\cdot}S{\cdot}Et + H_2 = 2EtSH$ when the mercaptan is added to a sugar–yeast fermentation mixture. The mercaptan was isolated in the form of a pure lead salt.

S. B. S.

Phytochemical Reductions. XII. The Conversion of Citronellal into Citronellol. PAUL MAYER and CARL NEUBERG (*Biochem. Zeitsch.*, 1915, **71**, 174—179).—The above reduction takes place when citronellal is added to a yeast-fermentation mixture, the process being the same as many other reductions of aldehydes to alcohols, as described by Neuberg and his collaborators. The citronellol was isolated, and identified by the preparation of the silver salt of the phthalyl ester, m. p. 123°, after recrystallisation from methyl alcohol. S. B. S.

The Reducing Enzymes of Dried Yeast (Lebedev) and of Rabbit Muscle. ARTHUR HARDEN and ROLAND VICTOR NORRIS (*Biochem. J.*, 1915, **9**, 330—336).—The power of reducing methylene-blue is restored to washed, dried yeast by a number of oxidisable substances, but not by others. Lactic acid is in the former list, and is oxidised to acetaldehyde, but the yield is less than the lactic acid lost. Probably pyruvic acid is an intermediate product; this is decomposed by the yeast-carboxylase into acetaldehyde and carbon dioxide. Washed rabbit's muscle also loses its power to reduce methylene-blue, and this is restored by various substances; but the enzyme concerned is different from that in yeast, since acetaldehyde restores the power to washed muscle, but not to washed, dried yeast. W. D. H.

An Oxalic Acid Producing Penicillium. JAMES N. CURRIE and CHARLES THOM (*J. Biol. Chem.*, 1915, **22**, 287—293).—*P. oxalicum* forms oxalic acid as the chief product of its metabolism, but less rapidly than *Aspergillus niger*. The biological significance of this is still obscure. W. D. H.

Normal and Abnormal Permeability. W. J. V. OSTERHOUT (*Amer. J. Bot.*, 1915, **2**, 93—94).—The permeability in sea-water, regarded as the normal permeability of *Laminaria*, whilst less than that in sodium chloride, is not the minimum permeability, and the resistance in sea-water is not the maximum, so that it is not correct to speak of the "normal permeability" of protoplasm to salts unless by "permeability" merely a rate of penetration considerably lower than that found in dead cells is meant. N. H. J. M.

Extreme Alterations of Permeability without Injury. W. J. V. OSTERHOUT (*Bot. Gaz.*, 1915, **59**, 246—253).—By the employment of quantitative methods, it is shown that the permeability of protoplasm may be increased to 20% above normal, and decreased to 39% below normal, without causing injury.

In the course of metabolism, a great number of substances are produced which affect the permeability of protoplasm, so that under normal conditions considerable fluctuations in permeability may occur. The whole course of metabolism may be controlled in this manner, since it depends on the exchange of substances between the cell and its environment. N. H. J. M.

Decrease of Permeability Due to Certain Bivalent Cations. W. J. V. OSTERHOUT (*Bot. Gaz.*, 1915, **59**, 317—330).—It is shown that whilst no univalent cation (except H) is able to decrease permeability, all the bivalent cations investigated (Mg, Ca, Ba, Sr, Mn, Co, Fe, Ni, Zn, Cd and Sn) produce marked depressions. N. H. J. M.

Assimilation of Carbon Dioxide by Plants. P. N. RAIKOW (*Chem. Zeit.*, 1915, **39**, 657—659). —A new theory of the assimilation

of carbon dioxide, based chiefly on the properties of chlorophyll and the presence in water of the oxonium compound $H_2O{:}OH_2$ or $H_2O{:}H(OH)$. The initial process is the production from chlorophyll (Ch), carbon dioxide, and water of a compound $Ch{:}O{:}C{:}OH_2$, which in presence of light at once changes to $Ch{:}OH{\cdot}CH{:}O{:}O$. This, under the influence of light, parts with oxygen, yielding $Ch{:}OH{\cdot}CH$, which again forms an oxonium compound with chlorophyll and the group $H{-}O{-}\overset{|}{C}{-}H$.

Simultaneously with the liberation of oxygen, the remaining complex may decompose into chlorophyll and *iso*formaldehyde. It is, however, considered more probable that chlorophyll is in part liberated, and that the rest polymerises.

The production of *iso*formaldehyde as the first product of assimilation, instead of formaldehyde, renders the explanation of the formation of carbohydrates more easy than is the case with Baeyer's theory. The production of fructose, for example, is to be expected as a consequence of the power of *iso*formaldehyde to form aldopentoses. It also makes possible the formation of pentoses as primary products instead of secondary products from hexoses.

According to the oxonium theory, half of the oxygen which is liberated is derived from carbon dioxide and half from water.

N. H. J. M.

The Properties of a Chromogen Universally Distributed in Plants. J. WOLFF and (MLLE.) NADIA ROUCHELMANN (*Compt. rend.*, 1915, **161**, 399—401).—A continuation of the study of the chromogen already described (this vol., i, 632). A large number of families of plants have been examined, and the chromogen found to be present. It turns brown under the influence of laccase or of carbonates of the alkalis or alkaline earths. When it is heated with sulphuric acid and resorcinol, and the product diluted with water and made alkaline, the resulting liquid is strongly fluorescent. The reaction with laccase and hydriodic acid (*loc. cit.*) is prevented by the presence of quercitannin. The presence of the chromogen prevents the oxidation of guaiacol by laccase. The authors do not agree with Palladin's views that the chromogens exist in the plants in the form of prochromogens or glucosides (compare A., 1910, i, 760), since the glucosides populin, solanin, arbutin, amygdalin, and salicin do not give the reactions for this chromogen, whilst extracts of the plants from which these glucosides come do give the reactions. Guaiacol is the only well-defined aromatic compound which approaches the chromogen in its sensitiveness to the combined action of laccase and hydriodic acid.

W. G.

Organic Chemistry.

The Preparation of Ethyl Bromide. Frank Edwin Weston (T., 1915, **107**, 1489—1490).—The author has worked out the best conditions for the preparation of ethyl bromide; these are to avoid any excess of alcohol, or a high temperature, and to use sodium bromide in place of the more expensive potassium salt.

Absolute alcohol (1 mol.), mixed with 5—10% of its weight of water, is treated in the cold with sulphuric acid (1 mol. + 5%) and to the cold mixture very coarsely powdered sodium bromide (1 mol.) is added. A 2-litre flask is sufficient to take 6 gram-molecular weights of the reagents. The mixture is heated very gently, first on a water-bath and then on a sand-bath, the rise in temperature being carefully regulated so as just to maintain a steady distillation of ethyl bromide and to prevent frothing. The only loss is of hydrogen bromide at the commencement of the heating, the yield of purified ethyl bromide, b. p. 38·5—39·5°, being 80—90% of the theoretical. D. F. T.

Preparation of Acetic Anhydride. Bosnische Electricitäts-A.-G. (*Eng. Pat.*, 23190, Nov., 1914; from *J. Soc. Chem. Ind.*, 1915, **34**, 982).—Acetic anhydride is formed when ethylidene diacetate is heated sufficiently above its boiling point, especially in the presence of a catalyst. Thus, when 100 grams of vaporised ethylidene diacetate, b. p. 169°, are conducted through a tube filled with pieces of pumice, at 250—300°, at the rate of 70 grams per hour for each litre of tube capacity, the product contains acetaldehyde (25·3%) acetic acid (17·1%) acetic anhydride (49%), and unchanged material (7%). The yield of pure acetic anhydride obtained after a fractionation is 43 grams.

J. C. W.

Catalytic Hydrogenation of Fatty Acids. H. Dubovitz (*Chem. Zentr.*, 1915, i, 1301—1302; from *Seifensieder Zeit.*, 1915, **42**, 304—306).—A laboratory method for the hydrogenation of oleic acid is described. The hydrogen employed is prepared from arsenic-free zinc and is purified by passing it successively through a mixture of ferric oxide and sawdust, potassium dichromate and sulphuric acid, sodium hydroxide solution, a tube containing palladium, and concentrated sulphuric acid. The catalyst is obtained by dissolving 50 grams of nickel nitrate in hot water, adding pumice-stone washed previously with hydrochloric acid and ignited, evaporating the mixture, and igniting the residue in a nickel basin until all nitric acid has been expelled; the ignited residue is then packed into a tube 163 cm. in length. The oleic acid, dried previously at 110°, is contained in a flask connected with one end of the tube, the air is exhausted from the whole apparatus, and the hydrogen then passed through the oleic acid heated at 270°; the tube containing the catalyst is heated at 300—350°, the nickel oxide having been reduced in a current of hydrogen under reduced pressure at 100°. The hydrogen bubbling through the oleic acid carries with it a quantity of oleic acid vapour (a low pressure

being maintained in the apparatus) and the gaseous mixture passes into the tube containing the catalyst, where hydrogenation of the acid takes place. W. P. S.

The β-Lactone of *as*-Dimethylmalic Acid. ERWIN OTT (*Ber.*, 1915, **48**, 1350—1353).—In extension of the earlier work (Ott, A., 1913, i, 1302) on the fission of certain β-lactonic esters, the behaviour of the methyl ester of the β-lactone of *as*-dimethylmalic acid has been examined.

The β-lactone, $CO<^{--O--}_{CMe_2}>CH\cdot CO_2H$, was converted through its ammonium and silver salts into the *methyl* ester, b. p. 70—72°/0·04 mm. When distilled under a pressure of 18 mm., decomposition occurred to an appreciable extent with formation of carbon dioxide and methyl ββ-dimethylacrylate, the most marked effect being produced by distillation in a vacuum over a feebly glowing platinum spiral. No indication was observable of the formation of dimethylketen, which would be expected if the decomposition even in part followed a course analogous to that observed with the isomeric series (*loc. cit.*). The relative position of the carbonyl group in the structures

$$\begin{array}{l} CO\text{---}O \\ | \\ CMe_2\cdot CH\cdot CO_2Me \end{array} \quad \text{and} \quad \begin{array}{l} O\text{---}CO \\ | \\ CMe_2\cdot CR\cdot CO_2Me \end{array}$$

thus appears to decide the course of the fission. D. F. T.

A New Oxidation Product of Cholic Acid. HANS PRINGSHEIM (*Ber.*, 1915, **48**, 1324—1327).—By oxidation of cholic acid in warm potassium hydroxide solution with bromine the author has obtained *biliobanic acid*, $C_{22}H_{30}O_7$, needles, m. p. near 285°, α_D^{20} + 22·4° in *N*-sodium hydroxide solution; the molecular weight in urethane is in accord with the formula given. The new acid could not be made to react with the usual reagents for ketonic substances, and in this resembles cilianic acid (Schenck, A., 1913, i, 1042), which is an oxidation product obtained from cholic acid with hot alkaline potassium permanganate solution. D. F. T.

Preparation of Salts of Formaldehyde-sulphurous Acid with Aluminium Oxide. CHEM. FABR. VON HEYDEN (*U.S. Pat.*, 1149712; from *J. Soc. Chem. Ind.*, 1915, **34**, 962).—Equimolecular proportions of aluminium oxide, formaldehyde, and sulphurous acid form a soluble salt, from which sodium carbonate precipitates aluminium hydroxide and strong acids expel sulphur dioxide. J. C. W.

Preparation of Acetaldehyde from Acetylene. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (*U.S. Pats.*, 1151928 and 1151929; from *J. Soc. Chem. Ind.*, 1915, **34**, 1031).—Acetylene is oxidised by a mercury compound in the presence of a substance capable of impeding the separation of mercury, such as a ferric salt (sulphate) or a sexavalent chromium compound (chromic acid). J. C. W.

Alkamines and a Process for Producing Same. ELI LILLY & Co. (*U. S. Pat.*, 1150251; from *J. Soc. Chem. Ind.*, 1915, **34**, 982).—Alkamines of the general formula,

$$NXX'\cdot CH_2\cdot CY(OH)\cdot[CH_2]_4\cdot CH_3,$$

in which X and X′ are alkyl radicles or hydrogen, and Y is a univalent group which can be introduced by means of its organomagnesium haloids, are prepared by treating chloromethyl ω-bromopropyl ketone with magnesium alkyl haloids and condensing the tertiary carbinols so formed with substituted amines. Special claim is made for dimethylaminomethylethyl-*n*-amylcarbinol, $NMe_2 \cdot CH_2 \cdot CEt(OH) \cdot [CH_2]_4 \cdot CH_3$.

J. C. W.

Alkamine, and a Process for Producing Same. ELI LILLY & Co. (*U.S. Pat.*, 1150252; from *J. Soc. Chem. Ind.*, 1915, **34**, 982).—Epichlorohydrin is treated with organomagnesium haloids, the resulting secondary alcohols are oxidised to ketones, these are again treated with Grignard compounds, and the tertiary carbinols are then condensed with substituted amines. For example: epichlorohydrin is treated with magnesium *iso*butyl bromide, the chloromethyl*iso*amyl carbinol is oxidised to the ketone, this is converted into chloromethylethyl*iso*amylcarbinol by the agency of magnesium ethyl bromide, and, finally, the tertiary alcohol is condensed with dimethylamine, to form dimethylaminomethylethyl*iso*amylcarbinol,

$$CHMe_2 \cdot CH_2 \cdot CH_2 \cdot CEt(OH) \cdot CH_2 \cdot NMe_2.$$

J. C. W.

Alkamine Esters, and Process for Producing Same. ELI LILLY & Co. (*U.S. Pat.*, 1150253: from *J. Soc. Chem. Ind.*, 1915, **34**, 982).—Dimethylaminomethylethyl*iso*amylcarbinol (preceding abstract) is acylated. The benzoate is specially claimed. The alkamine esters are local anæsthetics. J. C. W.

Esters of Alkamines and Process for Producing Same. ELI LILLY & Co. (*U.S. Pat.*, 1150580; from *J. Soc. Chem. Ind.*, 1915, **34**, 983).—Esters of the formula $NXX^1 \cdot CH_2 \cdot CZ(OY) \cdot [CH_2]_4 \cdot CH_3$, in which X and X^1 are alkyl groups or hydrogen, Y is an acid radicle, and Z is a univalent group which can be introduced by the Grignard reaction, are claimed. Particular mention is made of the benzoate of dimethylaminomethylethyl-*n*-amylcarbinol,

$$NMe_2 \cdot CH_2 \cdot CEt(OBz) \cdot [CH_2]_4 \cdot CH_3.$$

J. C. W.

Reactions in Liquid Ammonia. II. 1. Action of Acid Amides on the Amides, Imides, and Nitrides of Certain Heavy Metals. 2. Metallic Salts of Acid Ammono-esters. EDWARD C. FRANKLIN (*J. Amer. Chem. Soc.*, 1915, **37**, 2279—2295).—Franklin and Stafford (A., 1902, i, 748) have shown that certain acid amides and potassamide interact in liquid ammonia solutions in a manner analogous to the interaction of acids and bases in aqueous solutions, and Franklin (A., 1905, ii, 581) has formulated a system of acids, bases, and salts on the basis of ammonia as the typical substance.

It has now been found that the amide of silver, the imides of lead and copper, and the nitride of thallium dissolve in liquid ammonia solutions of acetamide, benzenesulphonamide, and *p*-toluenesulphonamide to form

well-crystallised, metallic derivatives of the acid amides. *Silver-acetamide*, $CH_3{\cdot}CO{\cdot}NHAg$, is formed by the action of acetamide on silver amide, thus:

$$AgNH_2 + CH_3{\cdot}CO{\cdot}NH_2 = CH_3{\cdot}CO{\cdot}NHAg + NH_3;$$

it crystallises from cold liquid ammonia as the *diammonate*,

$$CH_3{\cdot}CO{\cdot}NHAg,2NH_3.$$

Thallous-acetamide, $CH_3{\cdot}CO{\cdot}NHTl$, obtained from acetamide and thallous nitride, also furnishes a *diammonate*. The following compounds are also described. *Lead-acetamide*; *silver-benzenesulphonamide*, $C_6H_5{\cdot}SO_2{\cdot}NHAg$, and its *mono-* and *di-ammonates*; *thallous-benzenesulphonamide*,

$$C_6H_5{\cdot}SO_2{\cdot}NHTl,$$

and its *mono-* and *di-ammonates*; *thallous-p-toluenesulphonamide*, $C_6H_4Me{\cdot}SO_2{\cdot}NHTl$, and its *ammonate*; *cuprous-p-toluenesulphonamide diammonate*, $C_6H_4Me{\cdot}SO_2{\cdot}NHCu,2NH_3$; *cupric-p-toluenesulphonamide*, $(C_6H_4Me{\cdot}SO_2{\cdot}NH)_2Cu$; *cuprous-benzenesulphonamide*, $C_6H_5{\cdot}SO_2{\cdot}NHCu$, and its *diammonate*; *cupric-benzenesulphonamide tetrammonate*,

$$(C_6H_5{\cdot}SO_2{\cdot}NH)_2Cu,4NH_3,$$

and the *heptammonate*.

It is shown that such compounds as acetanilide and benzylacetamide are to be regarded as acid ammono-esters which in liquid ammonia solutions react with ammono-bases, just as acid amides do, to form ammono-salts. By the action of silver amide on acetanilide in liquid ammonia solution, *silver-acetanilide*, $CH_3{\cdot}CO{\cdot}NPhAg$, is produced; its *ammonate* was also prepared. *Thallous-acetanilide*, $CH_3{\cdot}CO{\cdot}NPhTl$, *potassium-acetobenzylamide ammonate*, $CH_3{\cdot}CO{\cdot}N(CH_2Ph)K,NH_3$, and *potassium-aceto-p-phenetidide*, $CH_3{\cdot}CO{\cdot}N(C_6H_4{\cdot}OEt)K$, are also described. E. G.

Preparation of Carbamide. BADISCHE ANILIN- & SODA-FABRIK. (*Eng. Pat.*, 24117, Dec., 1914; from *J. Soc. Chem. Ind.*, 1915, **34**, 924).—The mixture of the compounds of carbon dioxide with ammonia is heated in an autoclave, and the product is then transferred to a vacuum still and heated at about 75°. The unchanged ammonium compounds distil as carbon dioxide and ammonia and reunite in the cooled receiver, leaving carbamide and water in the still. The water is then removed by continuing the vacuum distillation, after changing the receiver. J. C. W.

Ring Formation. I. The Kaufler Formula for Derivatives of Diphenyl. EUSTACE EBENEZER TURNER (T., 1915, **107**, 1495—1500).—The author has obtained results which, although not necessarily disproving Kaufler's formula for diphenyl (A., 1907, i, 307, 794; also Cain, T., 1914, **105**, 1437), are difficult to reconcile with that view of the structure of diphenyl.

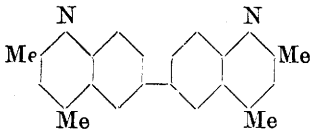
Although 2:2′-dibromodiphenyl reacts with sodium, producing *o*-diphenylene (Dobbie, Fox and Gauge, T., 1911, **99**, 963), 4:4′-dibromodiphenyl fails to give any *p*-diphenylene under similar conditions, a result which does not seem to accord well with the idea that the 4:4′-positions in diphenyl approach more closely than the 2:2′-positions. Also the 4:4′-dinitrodiphenyl derivatives, on treatment with sodium amalgam, show no tendency to form a closed ring con-

taining an azo- or azoxy-group, whereas 2 : 2′-dinitrodiphenyl does so (Täuber, A., 1891, 570).

The evidence produced by Cain (*loc. cit.*) in the ready condensation of α-diketones such as benzil with benzidine whilst phenanthraquinone fails to give such a reaction, is weakened by the fact that acetylacetone refuses to form a cyclic compound with benzidine. When benzidine is warmed with an excess of acetylacetone, a vigorous reaction sets in with formation of *diacetyl*iso*propylidenebenzidine*,

$$C_{12}H_8(N{:}CMe{\cdot}CH_2{\cdot}COMe)_2,$$

pale yellow or brown crystals, m. p. 198°; *tetrabromide*, colourless needles. When the condensation product is warmed with sulphuric acid, 2 : 4 : 2′ : 4′-tetramethyl-6 : 6′-diquinolyl (annexed formula) is produced. If the interaction of benzidine and acetylacetone is so effected in boiling xylene solution that the former reagent is always present in considerable excess, only one amino-group is attacked, the product being *monoacetyl*iso*propylidene benzidine*,



$$NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}N{:}CMe{\cdot}CH_2{\cdot}COMe,$$

pale yellow crystals, m. p. 137°; *hydrochloride*, colourless; *platinichloride*, prepared only with cold solutions, yellow, crystalline solid; *picrate*, yellow needles of no definite m. p. This condensation product resembles the diacetyl*iso*propylidene derivative in stability towards alkali and in ready hydrolysis by acids. D. F. T.

Some Crystallographic Properties of Aniline Nitrate. Frédéric Wallerant (*Compt. rend.*, 1915, **161**, 479—480).—Aniline nitrate, orthorhombic at the ordinary temperature, crystallises from water in very flat plates parallel to the faces g', the plane of easy cleavage, and the plane of the optical axes. The faces m and $b^1/_2$ are, on the contrary, very reduced. Crystallised from alcohol, the crystals are octahedra, showing only the faces $b^1/_2$ without traces of faces g'. It is a further example showing that the frequency and development of a face depend essentially on the conditions of crystallisation. Further, aniline nitrate is dimorphous, being transformed at 97·6° into monoclinic crystals, showing striations parallel to one plane under the influence of pressure. The transformation is reversible and indirect. A plate having orthorhombic cleavage, on heating at 97·6° is converted into monoclinic fibres not having any orientation, which on cooling are transformed, assuming the first orientation. This change takes place without superheating or crystalline superfusion, with quite a noticeable development of heat. W. G.

The Constitution of the Salts of Benzylideneanilines. A. Hantzsch (*Ber.*, 1915, **48**, 1340—1344).—In reply to Franzen and Henglein (this vol., i, 230), who favour the structure CHRCl·NHR for the hydrochlorides of the benzylideneanilines, the author insists on the character of these as true ammonium salts of the formula CHR:NRHCl, and suggests explanations for the abnormal behaviour of the salts and dibromides of these bases. D. F. T.

Stereochemistry of Quinquevalent Nitrogen. III. Autoracemisation of Optically Active Ammonium Compounds. SHIGERU KOMATSU (*Mem. Coll. Sci., Kyoto Imp. Univ.*, 1915, **1**, 231—248. Compare A., 1913, i, 39).—With a view of discovering the cause and the mechanism of autoracemisation in optically active ammonium compounds, the author has determined, polarimetrically, the velocity of inversion of certain iodides. In chloroform which had been kept in the dark in a cold place for a year, the results were the following:—(1) γ-*d*-phenylbenzylmethylallylammonium iodide, at 25°, had $k=0{\cdot}0017$, (2) at 30°, $k=0{\cdot}0038$; (3) γ-*l*-phenylbenzylmethylallylammonium iodide, at 25°, had $k=0{\cdot}0014$; (4) α-*d*-phenylbenzylmethylallylammonium iodide, at 25°, had $k=0{\cdot}0019$, and (5) at 30°, $k=0{\cdot}0023$; *l*-phenylbenzylmethyl-*n*-propylammonium iodide, at 25°, had $k=0{\cdot}0016$. In chloroform which had been treated with water, with sulphuric acid, and distilled, (6) α-*d*-phenylbenzylmethylallylammonium iodide, at 25°, had $k=0{\cdot}0014$, whilst in this same chloroform, after it had been made $N/2000$ with hydrogen chloride, (7) at 25°, $k=0{\cdot}0012$. The inversion of α-*d*-phenylbenzylmethylallylammonium iodide was also examined (9) in allyl alcohol at 25°; and that of *l*-phenylbenzylmethyl-*n*-propylammonium iodide at 25° in (10) acetonitrile, and in alcohol containing 20 per cent. of the following substances, (11) amylene, (12) α-crotonic acid, (13) butyric acid, (14) carbon tetrachloride, (15) acetylene dichloride, (16) chlorobenzene. The fact that the inversion constants of α- and γ-*d*-phenylbenzylmethylallylammonium iodide in chloroform are the same, whilst their specific rotations are different, is considered to support Halban's decomposition theory rather than Pope's dissociation theory. The ultraviolet absorption spectra of (1) a freshly-prepared chloroform solution of *d*-phenylbenzylmethylallylammonium iodide, [2] the same solution after keeping for a day, and (3) an equivalent solution of methylallylaniline, were photographed. The results are regarded as substantiating the above view that when α- and γ-*d*-phenylbenzylmethylallylammonium iodides are dissolved in chloroform, they decompose into methylallylaniline and benzyl iodide, the decomposition products then recombining to form γ-*r*-phenylbenzylmethylallylammonium iodide. Some other decomposition experiments are also held to support this conclusion. Since the value of the constant in experiments (1), (2), (4), and (7), above, is practically the same, it is considered that the primary cause of the reaction is to be ascribed to the solvent itself, and not to any catalytic action of halogen acid derived from the chloroform or from other impurities present in it. The effect of different solvents on the velocity of the change is indicated by the time (in hours) required for half change: chloroform, 3; amylene, 3; chlorobenzene, 48; carbon tetrachloride, 49; acetylene dichloride, 52; acetonitrile, 53; crotonic acid, 58; allyl alcohol, 119. From this it is concluded that the decomposition of the optically active substance is caused by the residual affinity of the solvents due to the presence of a multivalent element or unsaturated linking. Cooling curves are also given for *d*- and *r*-α-phenylbenzylmethylallylammonium iodide.

T. S. PA.

Metaquinonoids. EUG. BAMBERGER (*Ber.*, 1915, **48**, 1354—1357). —In an endeavour to decide the structure of the *o*-diazoxides produced by diazotising *o*-aminophenols, the author has attempted to prepare similar compounds from *m*-aminophenols. The entire lack of success is possibly connected with the impossibility of producing a hexacyclic metaquinonoid and so may be regarded as evidence in favour of the structure $O{:}C_6H_4{:}N_2$ for the *o*-diazoxides.

2 : 4 : 6-Tribromo-*m*-nitrophenol, when reduced with tin and hydrochloric acid, yields only *m*-aminophenol, no tribromo-*m*-aminophenol being obtained, although a little of the latter is produced if reduction is effected with iron and acetic acid. 2 : 4 : 6-Tribromo-*m*-aminophenol is best prepared by bromination of *m*-aminophenol in acetic acid, the m. p. being 119° instead of that accepted hitherto; diazotisation under various conditions gave no indication of the formation of a diazoxide.

Treatment of 4 : 6-dinitro-*m*-aminophenol in alcoholic suspension with nitrous gases gave rise to the formation of 2 : 4-*dinitroresorcinol monoethyl ether*, $OH{\cdot}C_6H_2(NO_2)_2{\cdot}OEt$, yellow prisms, m. p. 122—122·5°, the constitution of which was determined by conversion into 2 : 4-dinitroresorcinol by heating with hydrochloric acid at 180—200°.

D. F. T.

Some Homologues of Menthol. EYVIND BŒDTKER (*Bull. Soc. chim.*, 1915, [iv], **17**, 360—367).—The author has prepared a number of homologues of menthol by reducing the corresponding derivatives of menthone by means of sodium in ether saturated with water. The following are described :

Methylmenthol, $C_{11}H_{21}{\cdot}OH$, a viscid liquid, b. p. 129—130°/32 mm.; D_4^{18} 0·9124; n_D^{20} 1·4692; $[\alpha]_D^{21}$ −2°26′, giving with acetic anhydride an *acetate*, b. p. 125°/17 mm.; D_4^{18} 0·9313; n_D^{20} 1·4578; $[\alpha]_D^{22}$ −18°7′.

Ethylmenthol, $C_{12}H_{23}{\cdot}OH$, b. p. 124°/13 mm.; D_4^{18} 0·9246; n_D^{20} 1·4769; $[\alpha]_D^{22}$ +4°55′, giving an *acetate*, b. p. 131—132°/14 mm.; D_4^{18} 0·9366; n_D^{20} 1·4636; $[\alpha]_D^{21}$ −6°6′.

Propylmenthol, $C_{13}H_{25}{\cdot}OH$, b. p. 141—145°/27 mm.; D_4^{18} 0·9075; n_D^{20} 1·4675; $[\alpha]_D^{22}$ +29°7′, giving an *acetate*, b. p. 152°/30 mm.; D_4^{18} 0·9515; n_D^{19} 1·4741; $[\alpha]_D^{22}$ +8°58′.

iso*Amylmenthol*, $C_{15}H_{29}{\cdot}OH$, a clear liquid, b. p. 150°/23 mm.; D_4^1 0·8985; n_D^{20} 1·4661; $[\alpha]_D^{22}$ +33°44′.

Benzylidenementhone, $C_8H_{16}\begin{cases}C{:}CHPh\\ CO\end{cases}$, when reduced in the same way, gave benzylmenthol, $C_{17}H_{25}{\cdot}OH$, b. p. 203—205°/24 mm.; D_4^{20} 0·9819; n_D^{20} 1·5257; $[\alpha]_D^{20}$ −43°19′ (compare Semmler, A., 1904, i, 260).

Benzylmenthone, b. p. 177°/8 mm.; D_4^{18} 0·9979; n_D^{19} 1·5232; $[\alpha]_D^{23}$ +28°4′, was prepared from benzyl chloride and menthone by Haller's method (compare A., 1904, i, 600), a small quantity of the *dibenzyl* derivative, m. p. 52°, being obtained at the same time. All the above rotations were obtained in benzene solution.

W. G.

Preparation of Derivatives of 8-Amino-β-naphthol. BADISCHE ANILIN- & SODA-FABRIK (*Eng. Pat.*, 8058 of 1915; from *J. Soc. Chem. Ind.*, 1915, **34**, 828).—Halogenated 8-benzoylamino-β-naphthols, containing halogen in the benzene nucleus only, are prepared by the action of a halogenated benzoyl chloride, in the presence or absence of substances like sodium acetate which can fix hydrogen chloride. 8-*o*-Chlorobenzoylamino-β-naphthol is mentioned.

J. C. W.

Action of Magnesium Phenyl Bromide on Tellurium Dihaloids. KARL LEDERER (*Ber.*, 1915, **48**, 1345—1350).—Tellurium dibromide reacts vigorously with an ethereal solution of magnesium phenyl bromide; by distillation of the product, diphenyl and diphenyl telluride can be obtained whilst the residue contains tellurium and diphenyl ditelluride. Tellurium chloride and iodide gave similar results, the yield reaching 70% of diphenyl telluride in the interaction of tellurium iodide and magnesium phenyl iodide.

Diphenyl ditelluride, the first organic ditelluride to be isolated, forms long, red fibres, m. p. 53—54°. When treated in alcoholic solution with sodium it decomposes partly into tellurium and diphenyl telluride, but also gives rise to some *phenyl telluromercaptan*, which was separated as the *mercury chloride* derivative, C_6H_5·Te·HgCl, a yellow, amorphous solid, decomp. near 90°. Oxidation with nitric acid converted the ditelluride into the mixed *anhydride* of nitric and phenyltellurinic acids, NO_3·TePhO, needles, m. p. 232—233°, from which by careful successive treatment with sodium hydroxide and hydrochloric acid, *phenyltellurinic acid*, TePhO·OH, was obtained as a white powder, m. p. 210—211°; the selenium analogues of these compounds have already been described (Krafft and Lyons, A., 1896, i, 304).

A solution of diphenyl telluride in benzyl bromide gradually deposits a crystalline mass of *diphenylbenzyltelluronium bromide*,

$$TePh_2Br{\cdot}CH_2Ph,$$

m. p. 90—91°, which is converted by silver hydroxide and water into the corresponding *hydroxide*, a yellow oil very soluble in water; this gives a sparingly soluble *picrate*.

D. F. T.

Reaction between Alkalis and Metol and Quinol in Photographic Developers. FRANCIS C. FRARY and ADOLPH H. NIETZ (*J. Amer. Chem. Soc.*, 1915, **37**, 2273—2279).—In the work on the single potential of developers (this vol., ii, 815) it was observed that the addition of quinol caused a change of 30 millivolts in the hydrogen potential of a solution containing sodium carbonate and sulphite. As this indicated a combination between the alkali and the reducing agent, it was considered that the hydrogen potentials might be applied to a study of the reactions which take place when the developer is mixed. Determinations of the hydrogen potentials of sodium hydroxide solutions and the hydrolysis constant of sodium carbonate (this vol., ii, 816) have supplied the data necessary for the purpose.

The investigations now described have indicated that in the reaction between sodium hydroxide and quinol, either a mono- or a di-quinoxide may be formed according to the conditions. In the case of sodium

carbonate and quinol, in the concentrations usually used for developers, most of the quinol would be converted into the monoquinoxide if sodium sulphite was not present. When sulphite and carbonate are both present, the quinol seems to be shared between them. Complete oxidation of a quinol developer can be effected without changing its alkalinity. In the absence of a sulphite, metol (1 mol.) seems able to combine with 3 mols. of sodium hydroxide. E. G.

Dialkyl*cyclo*hexadienes and their Carboxylic Acids. K. von Auwers and R. Hinterseber (*Ber.*, 1915, **48**, 1357—1376).—A re-examination of the earlier results (von Auwers and Hessenland, A., 1908, i, 550, 551) as to the structure of the dialkyl*cyclo*hexadiene and the diolefinic *cyclo*hexadienecarboxylic acid obtainable from 1 : 4-dimethyl-4-dichloromethyl-Δ^6-*cyclo*hexen-5-one (dichloropulenenone) by warming with alcoholic potassium hydroxide. The previous decisions as to structure are confirmed.

1 : 4-Dimethyl-$\Delta^{1:3}$-*cyclo*hexadiene-3-carboxylic acid ($\Delta^{1:3}$-dihydro-*p*-xylic acid) obtained by the action of alcoholic potassium hydroxide on dichloropulenenone, has m. p. 41—42°, b. p. 139—140°/14 mm., D_4^{20} 1·043, n_D^{20} 1·4927. When reduced in boiling amyl-alcoholic solution by sodium, this acid yielded 1 : 4-*dimethyl*-Δ^3-cyclo*hexene*-3-*carboxylic acid*, prisms or rhombohedra, m. p. 71°, b. p. 136—138°/14—15 mm., 244°/ord. pressure (*methyl* ester, a colourless oil, b. p. 77·5—79·5°/12 mm., 200°/ord. pressure, D_4^{20} 0·968, n_D^{20} 1·4577), the constitution of which is demonstrated by its oxidation with cold alkaline permanganate to *δ-acetyl-β-methylvaleric acid*, $C_8H_{14}O_3$ (p-*nitrophenylhydrazone*, orange coloured crystals, m. p. 194—195°). This result, together with the spectrochemical and other evidence, suggests that the *cyclo*hexadiene acid has the structure $CH_2<\begin{matrix}CMe=CH\\CH_2\cdot CMe\end{matrix}>C\cdot CO_2H$, in accordance with its description above. This acid can be converted into 1 : 4-dimethyl-$\Delta^{1:3}$-*cyclo*hexadiene by heating at 120—125° in a current of hydrogen or by treating its dibromide with sodium, the product having b. p. 135—136°, D_4^{20} 0·833, n_D^{20} 1·4804. Confirmatory evidence of the structure of this hydrocarbon is supplied by successive bromination and treatment with diethylaniline, when *p*-xylene is produced, and by oxidation with ozone to acetonylacetone.

Under similar treatment with alcoholic potassium hydroxide, 1-methyl-1-dichloromethyl-4-ethyl-Δ^3-*cyclo*hexen-2-one was converted into 1-methyl-4-ethyl-$\Delta^{1:3}$-*cyclo*hexadiene-3-carboxylic acid, b. p. 152·5—153°/13 mm., D_4^{20} 1·024, n_D^{20} 1·4965; 1-methyl-4-*iso*propyl-$\Delta^{1:3}$-*cyclo*hexadiene-3-carboxylic acid, m. p. 83—84°, b. p. 170°/12 mm. (*sodium* salt, pearly leaflets; *silver* salt, colourless; *ethyl* ester, b. p. 128°/11 mm., D_4^{20} 0·975, n_D^{20} 1·4987) was obtained in like manner. Final proof of the structure of the latter acid is still lacking.

The substance described as 1-methyl-4-*iso*propyl-$\Delta^{1\ 3}$-*cyclo*hexadiene (von Auwers, A., 1909, i, 596), on oxidation with ozone, gives rise to *αα*-dimethylacetonylacetone, so that if not identical with α-terpinene it must at least consist largely of this hydrocarbon. D. F. T.

Unsaturated Hydroaromatic Acids. K. von Auwers and W. Treppmann (*Ber.*, 1915, **48**, 1377—1388).—Dehydration of ethyl 1 : 3-dimethyl-Δ^3-*cyclo*hexen-5-ol-5-acetic acid,

$$CH_2<\begin{matrix}CMe=CH\\CHMe\cdot CH_2\end{matrix}>C(OH)\cdot CH_2\cdot CO_2Et,$$

gives rise to ethyl 1 : 3-dimethyl-Δ^3-*cyclo*hexenylidene-5-acetate,

$$CH_2<\begin{matrix}CMe=CH\\CHMe\cdot CH_2\end{matrix}>CH{:}CH\cdot CO_2Et,$$

(von Auwers and Peters, A., 1910, i, 841); the corresponding free acid, when reduced in sodium carbonate solution by sodium amalgam, is converted into 1 : 3-*dimethyl*-Δ^4-cyclo*hexenyl*-5-*acetic acid*,

$$CH_2<\begin{matrix}CHMe\cdot CH\\CHMe\cdot CH_2\end{matrix}>C\cdot CH_2\cdot CO_2H,$$

an oily substance, b. p. 159—160°/20 mm., D_4^{20} 0·993, n_D^{20} 1·4767; the *ethyl* ester, an oil, b. p. 114—115·4°/13·5 mm., D_4^{20} 0·938, n_D^{20} 1·4577, gives an oily *dibromide*; the *amide*, leaflets, m. p. 152—154°, was obtained by the action of aqueous ammonia on the *chloride*, the latter being prepared by treating the acid with thionyl chloride. The above decision as to the structure of the new acid was confirmed by oxidation, when an oily ketomonocarboxylic *acid* was obtained which gave a *silver* salt approximating to the composition $C_9H_{15}O_3Ag$. An endeavour was made to prepare the above acid in an independent manner by treating 1 : 3-dimethyl*cyclo*hexan-5-one with zinc and ethyl bromoacetate in the presence of benzene, the product being *ethyl* 1 : 3-*dimethyl*cyclo*hexan*-5-*ol*-5-*acetate*, $CH_2<\begin{matrix}CHMe\cdot CH_2\\CHMe\cdot CH_2\end{matrix}>C(OH)\cdot CH_2\cdot CO_2Et$, a viscous oil of pleasant aromatic odour, b. p. 137·5—139°/18 mm., D_4^{20} 0·985, n_D^{20} 1·4543, which when heated with potassium hydrogen sulphate at 160° gave ethyl 1 : 3-dimethyl-Δ^4-*cyclo*hexenyl-5-acetate as a colourless oil, b. p. 116°/14 mm., D_4^{20} 0·936, n_D^{20} 1·4580; this on hydrolysis gave the corresponding acid as a crystalline mass, leaflets, m. p. 56—57°, b. p. 150—151°/15 mm. D_4^{20} 0·993, n_D^{20} 1·4766, both in the supercooled condition. In spite of the agreement in the physical data, it was not found possible to cause the oily acid to crystallise by inoculating with a little of this solid product, but the identity of the two products appears to be demonstrated conclusively by the identity of the amide prepared from the two; the refusal of the former acid to crystallise is probably to be attributed to slight impurity.

In order to exclude the possibility of one of the above products being one of the likely isomerides, 1 : 3-*dimethyl*cyclo*hexan*-5-*ol*-5-*acetic acid*, prisms, m. p. 97—98°, was obtained by hydrolysis of its ethyl ester described above, and boiled with acetic anhydride, by which means 1 : 3-*dimethyl*cyclo*hexylidene*-5-*acetic acid*,

$$CH_2<\begin{matrix}CHMe\cdot CH_2\\CHMe\cdot CH_2\end{matrix}>C{:}CH\cdot CO_2H,$$

prisms, m. p. 126°, was prepared; *methyl* ester, a pleasant aromatic oil, b. p. 113—114°/14 mm., D_4^{20} 0·953, n_D^{20} 1·470; *ethyl* ester, b. p. 126—128°/15 mm., D_4^{20} 0·941, n_D^{20} 1·4723.

If 1 : 3-dimethyl-Δ^3-*cyclo*hexen-3-one is treated with zinc and ethyl α-bromopropionate, condensation occurs with formation of an ester, the

dehydration of which with potassium hydrogen sulphate yielded *ethyl* α-1 : 3-*dimethyl*-Δ^3-cyclo*hexenylidene*-5-*propionate*,

$$CH_2<\begin{matrix}CMe=CH\\CHMe\cdot CH_2\end{matrix}>C:CMe\cdot CO_2Et,$$

an oil, b. p. 136—138°/12 mm., D_4^{20} 0·969, n_D^{20} 1·5069, whilst in a similar manner from zinc, ethyl α-bromo*iso*butyrate, and dimethyl*cyclo*hexenone there was obtained *ethyl* α-1 : 3-*dimethyl*-$\Delta^{3:5}$-cyclo*hexadienyl*-5-iso*butyrate*, $CH_2<\begin{matrix}CMe=CH\\CHMe\cdot CH\end{matrix}>C\cdot CMe_2\cdot CO_2Et$, an oil, b. p. 141—142°/20 mm., D_4^{20} 0·963, n_D^{20} 1·4865. The corresponding free *acid*, obtained by saponification, formed hexagonal tablets, m. p. 114—115°; *silver* salt, sparingly soluble in water, very soluble in ether. D. F. T.

Hydroaromatic Cyanohydrins and α-Hydroxycarboxylic Acids. K. von Auwers and F. Krollpfeiffer (*Ber.*, 1915, **48**, 1389—1397).—The preparation of unsaturated cyclic hydrocarbons by elimination of carbon dioxide from the corresponding carboxylic acids is rendered of little practical value from the difficulties encountered in the production of these unsaturated carboxylic acids. The cyanohydrin synthesis can be effected with such compounds as 1 : 3-dimethyl-*cyclo*hexan-5-one but the hydrolysis of the resulting hydroxy-nitrile in certain cases, for example, that derived from 1-methyl*cyclo*hexan-2-one instead of yielding the corresponding carboxylic acid, merely eliminates hydrogen cyanide, regenerating the ketone and its condensation products. Another difficulty encountered in this method of preparing unsaturated cyclic hydrocarbons is in the unexpected resistance of the hydroxy-acids and their esters towards dehydrating agents, even under widely varied conditions; in such cases as permitted dehydration to proceed, the action was often so slow as to cause the resulting unsaturated acid or ester to undergo partial polymerisation. The most satisfactory dehydrating agent was sulphuric acid, which could, however, only be applied to the esters because, under its influence, the free acids decomposed into ketone and formic acid. Still less encouraging was an attempt to convert the final cyanohydrins into unsaturated nitriles to be subsequently hydrolysed, as the final yields of acids were very small.

From the cyanohydrin of *cyclo*hexanone, *cyclo*hexan-1-ol-1-carboxylic acid and its ethyl ester were obtained; the latter forms needles or prisms, m. p. 20—22°, b. p. 99—101°/15 mm. D_4^{20} 1·044, n_D^{20} 1·4554 (compare Tarbouriech, A., 1909, i, 796); the corresponding amide was also obtained, m. p. 128—129°.

The *cyanohydrin* derived from 1-methyl*cyclo*hexan-2-one, was a pale yellow oil which decomposed when distilled in a vacuum and resisted all attempts at hydrolysis.

1 : 3-Dimethyl*cyclo*hexan-5-one yielded a *cyanohydrin* the hydrolysis of which produced 1 : 3-*dimethyl*cyclo*hexan*-5-*ol*-5-*carboxylic acid*, leaflets, m. p. 124—125°.

*cyclo*Pentan-1-ol-1-carboxylic acid, when heated with phosphoric oxide in benzene solution, gave *cyclo*pentene-1-carboxylic acid, the yield being only 10% of the theoretical. *Ethyl* cyclo*pentan*-1-*ol*-1-*carboxylate* is a

colourless, pleasant smelling liquid, b. p. 99°/20 mm., D_4^{20} 1·057, n_D^{20} 1·4498; the corresponding *methyl* ester, b. p. 85°/16 mm., gave D_4^{20} 1·102, n_D^{20} 1·4554. D. F. T.

Preparation of Magnesium Acetylsalicylate [*o*-Acetoxybenzoate]. Chemische Fabrik Gedeon Richter (*Eng. Pat.*, 10946, May, 1914; from *J. Soc. Chem. Ind.*, 1915, **34**, 982).—Magnesium oxide (40 grams) or hydroxide or carbonate, is stirred with *o*-acetoxybenzoic acid (360 grams) and water (180 grams) and, after some time, the mass is digested with methyl or ethyl alcohol. *Magnesium* o- *acetoxybenzoate* is then precipitated from the filtrate by means of ether, as a white, microcrystalline powder which is almost tasteless and readily soluble in water. J. C. W.

The Action of Nitrosylsulphuric Acid on *p*-Hydroxybenzoic Acid. J. Biehringer and W. Borsum (*Ber.*, 1915, **48**, 1314—1319).—The authors have submitted *p*-hydroxybenzoic acid to the action of nitrosylsulphuric (nitrosulphonic) acid, and have in this way extended the observations of Deninger (A., 1891, 307) on this reaction. A solution of sodium nitrite in sulphuric acid was added to a solution of *p*-hydroxybenzoic acid in the same liquid and the mixture was kept well stirred for 7 hours at 35—40°, after which it was left overnight. The chief product was 3-sulpho-4-hydroxybenzoic acid, accompanied by smaller quantities of 3-nitro-4-hydroxybenzoic acid and 2 : 4-dinitrophenol and possibly of 3 : 5-dinitro-*p*-hydroxybenzoic acid.

Further nitration of the 3-sulpho-4-hydroxybenzoic acid by treating a solution of the sodium salt in a mixture of acetic and sulphuric acids with fuming nitric acid gave 3 : 5-dinitro-4-hydroxybenzoic acid and dinitrophenol. D. F. T.

Tyrosine. Arthur Geake and Maximilian Nierenstein (*Biochem. J.*, 1915, **9**, 309—312).—Tyrosine is not affected by diazomethane, which indicates that not only are the amino-acid groups arranged in a betaine ring (compare A., 1914, i, 1057), but the hydroxyl group is rendered dormant by the nitrogen atom. Glycyl-*l*-tyrosine, in which the betaine ring is opened, yields the *methyl* ester,

$$OH\cdot C_6H_4\cdot CH_2\cdot CH(CO_2Me)\cdot NH\cdot CO\cdot CH_2\cdot NH_2,$$

m. p. 123—124°, but here again the phenolic group is protected from methylation.

In 3 : 4-dihydroxyphenylalanine, the meta-hydroxyl group should be open to methylation. The compound does react with diazomethane, but more material is required before a definite product can be described. J. C. W.

Nitrated Proteins. II. Synthesis of 3 : 5-Dinitrotyrosine. Treat B. Johnson and Edward F. Kohmann (*J. Amer. Chem. Soc.*, 1915, **37**, 2164—2170).—In connexion with the authors' work on nitrated proteins (this vol., i, 899), an attempt was made to prepare dinitrotyrosine by Städeler's method (*Annalen*, 1860, **116**, 82) but without success, and it is considered that the product obtained by Städeler probably consisted of impure nitrotyrosine. Dinitrotyrosine

can, however, be easily obtained by nitrating tyrosine with a mixture of nitric and sulphuric acids, and it is shown that the compound thus prepared has the nitro-groups in the 3- and 5-positions.

3 : 5-*Dinitrotyrosine*, $OH{\cdot}C_6H_2(NO_2)_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H,H_2O$, forms golden yellow plates; it does not lose its water of crystallisation at 110°, but when heated at 140—150° the water is expelled and the substance assumes a brick-red colour. It does not give a red coloration with Millon's reagent, but yields a yellow, insoluble *mercury* salt which begins to decompose at 170° and effervesces at 185°. The *hydrochloride* forms yellow plates and decomposes at 220—230°; the *ammonium* salt crystallises in red prisms and decomposes above 230°.

When 3 : 5-dinitrotyrosine is warmed with ammonium thiocyanate and acetic anhydride, it is converted into 4-(3 : 5-*dinitro*-4-*hydroxybenzyl*)-2-*thiohydantoin*, $OH{\cdot}C_6H_2(NO_2)_2{\cdot}CH_2{\cdot}CH<\begin{matrix}CO\text{—}NH\\|\\NH{\cdot}CS\end{matrix}$, m. p. 225—230° (decomp.), which crystallises in short prisms, and when heated with chloroacetic acid is desulphurised with formation of 4-(3 : 5-*dinitro*-4-*hydroxybenzyl*)-*hydantoin*,

$$OH{\cdot}C_6H_2(NO_2)_2{\cdot}CH_2{\cdot}CH<\begin{matrix}CO\text{—}NH\\|\\NH{\cdot}CO\end{matrix},$$

which forms golden-yellow blocks and decomposes at 235°. On reducing the latter compound with tin and hydrochloric acid, diazotising the resulting diaminohydantoin, and digesting the product with cuprous chloride solution, 4-(3 : 5-dichloro-4-hydroxybenzyl)-hydantoin (Wheeler, Hoffman, and Johnson, A., 1911, i, 923) is produced. E. G.

Studies in the Phenylsuccinic Acid Series. II. Some Derivatives of the Optically Active Diphenylsuccinic Acids. HENRY WREN and CHARLES JAMES STILL (T., 1915, **107**, 1449—1459; compare *loc. cit.*, 444).—An account of some of the derivatives of the *d*- and *l*-diphenylsuccinic acids described in the earlier communication.

Barium d-*diphenylsuccinate* forms well defined prisms with $5H_2O$, and resembles the corresponding salt of the racemic acid in its sparing solubility in water. *Methyl* r-*diphenylsuccinate* forms rhombic platelets, m. p. 173·5—174°; *methyl* meso-*diphenylsuccinate* forms needles, m. p. 218·5—219·5°; *methyl* d-*diphenylsuccinate* forms platelets, m. p. 165—166°, $[\alpha]_D^{16\cdot2}$ +341·9° in acetone, $[\alpha]_D^{15\cdot8}$ +376·8° in chloroform, whilst its lævo-isomeride possessed the same m. p. and has $[\alpha]_D^{15\cdot6}$ −342·1° in acetone, $[\alpha]_D^{14\cdot2}$ −365·3° in ethyl acetate, and $[\alpha]_D^{16\cdot3}$ −431·8° in carbon tetrachloride. *Ethyl* d-*diphenylsuccinate*, rectangular plates, m. p. 104—105°, gives $[\alpha]_D^{16}$ +279·4° in acetone solution, $[\alpha]_D^{15\cdot2}$ +281·3° in methyl alcohol, $[\alpha]_D^{18}$ +294·9° in ethyl acetate, and $[\alpha]_D^{18\cdot6}$ +305·5° in chloroform, whilst the l-*isomeride* gives $[\alpha]_D^{15\cdot4}$ −279·7° and $[\alpha]_D^{15\cdot4}$ −287·6° in acetone and ethyl alcohol respectively. In esterification of the *l*-acid by the Fischer-Speier method, *ethyl hydrogen* l-*diphenylsuccinate*, a bulky powder, m. p. 113·5—114·5°, $[\alpha]_D^{16\cdot5}$ −328·7° in acetone, $[\alpha]_D^{16\cdot8}$ −315·6° in ethyl alcohol, $[\alpha]_D^{13}$ −386·4° in carbon tetrachloride, was obtained as a by-product, being first isolated as the *sodium* salt; *ethyl sodium* d-*diphenylsuccinate* forms pearly leaflets with $4H_2O$.

d-Diphenylsuccinic acid is not appreciably racemised at 100° by aqueous potassium hydroxide, but considerable racemisation occurs during the hydrolysis of the optically active esters with aqueous-alcoholic potassium hydroxide, the first inactive product being the *meso*-acid.

Treatment with acetyl chloride or thionyl chloride converts the active diphenylsuccinic acids into the corresponding *anhydrides*, oblique prisms, m. p. 105·5—106·5°; the following figures were obtained with the *l*-anhydride, $[\alpha]_D^{17\cdot4}$ −287·7° in benzene, $[\alpha]_D^{18\cdot6}$ −285·4° in toluene, $[\alpha]_D^{20}$ −263·1° in ethyl acetate, $[\alpha]_D^{20\cdot4}$ −247·6° in carbon tetrachloride solution, whilst the *d*-anhydride gave $[\alpha]_D^{18\cdot5}$ +286·2° in benzene, and $[\alpha]_D^{20\cdot2}$ +246·0° in chloroform. These anhydrides react with hot water, giving active diphenylsuccinic acids of the same sign, but containing about 8% of an inactive acid consisting at least partly of the *meso*-acid, whilst with alcohol the product is in each case an ethyl hydrogen ester containing approximately 80% of the active form. D. F. T.

The Chromoisomerism of Salts of the Phenolaldehydes. A. HANTZSCH (*Ber.*, 1915, **48**, 1332—1338).—Polemical, in reply to the views of Pauly (this vol., i, 689), which do not accord with those of the author (this vol., i, 549). D. F. T.

The Action of Diazomethane on Some Aromatic Acyl Chlorides. DOUGLAS ARTHUR CLIBBENS and MAXIMILIAN NIERENSTEIN (T., 1915, **107**, 1491—1494).—An extension to acyl chlorides of the observations of Schlotterbeck (A., 1907, i, 185, 478; 1909, i, 553) and Meyer (A., 1907, i, 323) that aldehydes react with diazomethane, giving methyl ketones. The same reagent with acyl chlorides yields chloromethyl ketones, the reaction being effected in ethereal solution. ω-Chloroacetophenone and ω-bromoacetophenone were obtained in this manner from the corresponding acyl haloids. Phenylacetyl chloride gave rise to *benzyl chloromethyl ketone*, $CH_2Ph\cdot CO\cdot CH_2Cl$, stellar aggregates of needles, m. p. 72—73°. Phenylpropionyl chloride yielded *β-phenylethyl chloromethyl ketone*, $CH_2Ph\cdot CH_2\cdot CO\cdot CH_2Cl$, needles, m. p. 84—85°. Anisyl chloride gave anisyl chloromethyl ketone,

$$OMe\cdot C_6H_4\cdot CO\cdot CH_2Cl.$$

In the case of two *o*-acetoxyacyl chlorides which were examined, the primary product could not be isolated on account of the elimination of acetyl chloride with formation of a coumaranone. Thus *o*-acetoxybenzoyl chloride yielded coumaranone itself, $C_6H_4\langle{}^{O\text{—}}_{CH_2}\rangle CH_2$, whilst *2-acetoxy-4-methoxybenzoyl chloride*, $OMe\cdot C_6H_3(OAc)\cdot COCl$, prismatic needles, m. p. 81—82°, gave 3-methoxycoumaranone,

$$OMe\cdot C_6H_3\langle{}^{O\text{—}}_{CO}\rangle CH_2.$$

The necessary 2-acetoxy 4-methoxybenzoyl chloride was obtained from resorcinol by treating in sodium hydrogen carbonate solution with carbon dioxide, the process being a modification of that of Bistrycki and Kostanecki (A., 1885, 1037); the resulting β-resorcylic acid was then converted into 2-acetoxy-4-methoxybenzoic acid (m. p. 145—147°; Nagai, A., 1892, 58, gives 140°) by way of *p*-methoxysalicylic acid

In experiments on the action of diazomethane on triphenylcarbinol, benzhydrol, benzyl alcohol, and benzoylcarbinol, these substances were recovered unaltered ; benzilic acid and mandelic acid were converted into their respective methyl esters. D. F. T.

The Behaviour of Nitriles towards Organometallic Derivatives of Magnesium. EUSTACE EBENEZER TURNER (T., 1915, **107**, 1459—1464).—A marked case of steric hindrance appears to exist in the behaviour of 2 : 6-diethoxybenzonitrile towards organomagnesium haloids, variation of the reagent, the temperature, and the solvent all failing to effect any reaction, whilst benzonitrile reacts readily with this class of compounds.

p-Tolyl benzyl ketone can be obtained only in very poor yield by the action of magnesium *p*-tolyl iodide on phenylacetonitrile, the acidic character of the methylene group of the latter compound possibly interfering with the normal course of the reaction. By using magnesium benzyl chloride and *p*-toluonitrile in ethereal solution, *p*-tolyl benzyl ketone can be obtained in good yield, but in xylene solution the reaction takes an abnormal course, giving dibenzyl and *p-tolyl αβ-diphenylethyl ketone*, $C_6H_4Me\cdot CO\cdot CHPh\cdot CH_2Ph$, colourless needles, m. p. 90°, the identity of which was confirmed by synthesis from *p*-tolyl benzyl ketone, benzyl chloride, and sodium ethoxide in alcoholic solution. *p*-Tolyl *αβ*-diphenylethyl ketone is not affected by the usual reagents for a ketone; when prepared by the Grignard reaction in xylene solution as described above, it is accompanied by a *substance*, m. p. near 230°, and a magnesium salt of uncertain nature.

When *p*-tolyl benzyl ketone is heated with semicarbazide hydrochloride in alcoholic solution at 180° for three hours, a sparingly soluble *substance*, $C_{29}H_{28}N_2$, yellow needles, m. p. 181°, molecular weight in benzene and naphthalene between 400 and 450, was obtained, which on hydrolysis with hydrochloric or sulphuric acid regenerated the original ketone. D. F. T.

Indones. I. Synthesis of 3-Phenyl-2-ethylindone. R. DE FAZI (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 150—156, and *Gazzetta*, 1915, **45**, ii, 143—150).—The formation of 2 : 3-diphenylindone by the action of phosphoric oxide on *β*-hydroxy-*αββ*-triphenylpropionic acid (this vol., i, 542) indicates the possibility of obtaining derivatives of indone from cinnamic acid.

The interaction of ethyl *α*-bromobutyrate and benzophenone in presence of granulated zinc yields ethyl *β*-hydroxy-*ββ*-diphenyl-*α*-ethylpropionate (compare Schroeter, A., 1904, i, 415 ; 1907, i, 530 ; Rupe and Busolt, A., 1908, i, 23 ; Rupe, Steiger, and Fiedler, A., 1914, i, 281),

$$Ph\cdot COPh + CHEtBr\cdot CO_2Et + Zn = ZnBr\cdot O\cdot CPh_2\cdot CHEt\cdot CO_2Et,$$

and the latter $+ H_2O = ZnO + HBr + OH\cdot CPh_2\cdot CHEt\cdot CO_2Et$. With cold concentrated sulphuric acid, this ester gives a transitory yellow coloration, which changes rapidly to emerald green. Such a green coloration is, indeed, given by *β*-hydroxy-*αββ*-triphenylpropionic acid and by 2 : 3-diphenylindone ; by ethyl *β*-hydroxy-*ββ*-diphenyl-*α*-ethylpropionate and by 3-phenyl-2-ethylindone ; by ethyl *β*-hydroxy-*ββ*-

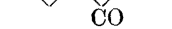
diphenyl-α-methylpropionate and by 3-phenyl-2-methylindone. That the coloration given by these acids with sulphuric acid is a sign of the formation of indones is confirmed by the results of Stoermer and Voht (this vol., i, 684), who found that α-methylcinnamic acid, which cannot be converted into 2-methylindone, gives no coloration with sulphuric acid in the cold, whereas *allo*-α-methylcinnamic acid, which gives a violet-blue coloration, is readily transformed into 2-methylindone; similar behaviour is shown by α-ethyl- and *allo*-α-ethylcinnamic acids. It should, therefore, be possible to synthesise indone by transforming cinnamic acid into *allo*-cinnamic acid and dehydrating the latter.

Graebe and Aubin (A., 1887, 589) used sulphuric acid to effect dehydration between a phenyl and a carboxyl group, obtaining diphenylene ketone from diphenyl-*o*-carboxylic acid. By similar means Roser and Haseloff (A., 1888, 1304) prepared 2 : 3-dibromoindone from αβ-dibromocinnamic acid, whilst Liebermann (A., 1898, i, 662), from *allo*cinnamic acid, obtained, not indone, but its dimeride, truxone.

By cold, concentrated sulphuric acid, ethyl β-hydroxy-ββ-diphenyl-α-ethylpropionate is first hydrolysed to the free acid, this then losing $1H_2O$, giving β-phenyl-α-ethylcinnamic acid, which undergoes dehydration to 3-phenyl-2-ethylindone :

$$OH\cdot CPh_2\cdot CHEt\cdot CO_2Et \longrightarrow OH\cdot CPh_2\cdot CHEt\cdot CO_2H \longrightarrow$$

$$CPh_2{:}CEt\cdot CO_2H \longrightarrow$$



This method of synthesising indones is simple to carry out and gives good yields.

Ethyl β-hydroxy-ββ-diphenyl-α-ethylpropionate, $C_{19}H_{22}O_3$, forms large, white needles, m. p. 107—108°. With concentrated sulphuric acid it gives, in the cold, an emerald green coloration, becoming deep yellow on dilution, and in the hot, a red coloration.

3-*Phenyl-2-ethylindone*, $C_{17}H_{14}O$, forms shining, orange-yellow prisms, m. p. 92—93°, and gives a green coloration with cold, and a red one with hot sulphuric acid, and a red coloration with cold, concentrated nitric acid. Its *oxime*, $C_{17}H_{15}ON$, forms long, golden-yellow needles, m. p. 182—183°, and gives a blood-red coloration with concentrated sulphuric acid in the cold; the *phenylhydrazone*, $C_{23}H_{20}N_2$, forms yellow prisms, m. p. 136—138°, and gives a reddish-brown coloration with sulphuric acid in the cold. T. H. P.

Preparation of 9-Benzoylfluorene. Wilhelm Wislicenus and Alfred Fehrle (*Ber.*, 1915, **48**, 1320—1323).—The authors have investigated the best conditions for the preparation of 9-benzoylfluorene, $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CHBz$, by the interaction of fluorene and an alkyl benzoate (compare Werner, A., 1906, i, 436), and have by the following method been able to obtain a yield of 80% of that theoretically expected from the fluorene.

A mixture of 14 grams of amyl benzoate, 2—4 grams of potassium shavings and 5 grams of fluorene is kept for one or two days and the

reaction is then completed by warming on a water-bath. The gelatinous reaction mixture is treated with alcohol to remove any excess of potassium and the benzoylfluorene can then be liberated by the addition of water and acetic acid. The product is accompanied by a small quantity of a yellowish-red substance, probably 1:4-bidiphenylenebutadiene (this vol., i, 519).

9-Benzoylfluorene could not be made to give a phenylhydrazone; the product of interaction with phenylhydrazine in acetic acid solution was a *substance*, $C_{26}H_{17}N$, yellow, rectangular plates, m. p. 217—218°, possibly of the structure $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}CPh\\C_6H_4\end{matrix}\!\!>\!N$, which under certain conditions was accompanied by a *substance*, almost black, crystalline grains, m. p. 150—155°, soluble in sulphuric acid, giving a violet-red coloration. D. F. T.

Preparation of 4-Halogeno-1-hydroxyanthraquinone and Substitution Products Thereof. F. Ullmann (*Eng. Pat.*, 14954, June, 1914; from *J. Soc. Chem. Ind.*, 1915, **34**, 952).—Phthalic anhydride, or a substitution product, is condensed with a *p*-halogenophenol, or a substitution product, by means of aluminium chloride, and the 5-halogeno-2-hydroxybenzoylbenzoic acid, or derivative, so obtained is converted into the anthraquinone compound by an agent such as sulphuric acid monohydrate. J. C. W.

Preparation of Arylsulphonylaminoanthraquinone-sulphonic and -carboxylic Acids. Aktien Gesellschaft für Anilin-Fabrikation (*Eng. Pat.*, 8109, June, 1915; from *J. Soc. Chem. Ind.*, 1915, **34**, 952).—Halogenoanthraquinone-sulphonic and -carboxylic acids are condensed readily with arylsulphonylamides in aqueous alkaline solution at 100°. The products are useful for the preparation of dyes. J. C. W.

Preparation of 2-Arylanthraquinonylthiocarbamides. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P., 254744; addition to 229111. Compare A., 1911, i, 469).—The formation of by-products in the condensation of 2-aminoanthraquinone with an aryl thiocarbimide is prevented by the use of a condensing agent, such as aluminium chloride. J. C. W.

Process for Hydrogenising Olefinic Terpene Alcohols, Aldehydes, and Terpenic Acids. C. Paal (*Eng. Pat.*, 16180, July, 1914; from *J. Soc. Chem. Ind.*, 1915, **34**, 982).—A claim is made for reduction with hydrogen under ordinary or increased pressures, in the presence of finely divided or colloidal metals of the platinum group, or of their protohydroxides in the non-colloidal state, deposited on finely divided inert substances which are not anti-catalytic, such as magnesium, nickel, cobalt, magnesium oxide, magnesium or calcium carbonate, barium sulphate, kieselguhr, carbon, sawdust, cellulose powder, etc. A number of examples is given. J. C. W.

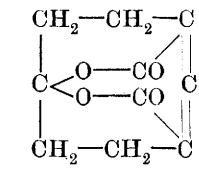
The Volatile Oil of Cymbopogon Senaarensis, Chiov. Oswald Digby Roberts (T., 1915, **107**, 1465—1470).—The above grass on distillation with steam was found to yield 1·2% of an oil, D_{15}^{15} 0·9422,

α_D^{23} +29·6°, acid number 4·2, ester number before acetylation 14·5, ester number after acetylation 62·1. In this oil were detected the following constituents:—acetic, decoic, and octoic acids in the free condition, also octoic, decoic and palmitic acids as esters (total approx. 2% of the oil); ketones (45%), perhaps entirely Δ^1-menthenone (bis*nitroso*-compound, $C_{20}H_{30}O_4N_2$, colourless crystals, m. p. 96—97° with decomp.), which on oxidation with neutral potassium permanganate solution gave α-hydroxy-α-methyl-α^1-*iso*propyladipic acid together with diosphenol and an *acid*, needles, m. p. 126—127°; phenolic substances (0·2%) yielding a *benzoyl* derivative, needles, m. p. 70—72°; a sesquiterpene *alcohol* (25%), $C_{15}H_{26}O$, b. p. 170—175°/21 mm., 280—285 at atmos. pressure, D_{15}^{15} 0·9544, α_D^{24} + 10·8°, having a faint resinous odour, which could be dehydrated by phosphoric oxide to a *sesquiterpene*, b. p. 150—155°/27 mm., D_{15}^{15} 0·9114, α_D^{23} + 24·4°, of no appreciable odour; an alcohol (3%) with a faint odour resembling that of geraniol; a terpene mixture (13%) in which *d*-limonene was detected; it also probably contained pinene; the residue (11·8%) probably contained squiterpenes. D. F. T.

Power of Colophony of Combining with its Solvents, especially with Petroleum Hydrocarbons. Ludwig Paul (*Chem. Zentr.*, 1915, ii, 189—190; from *Seifensieder Zeit.*, 1915, **42**, 393—395, 412—413, 434—435. Compare this vol., i, 828, 829).—When γ-pinic acid (KS acid) is ground with 90% alcohol and the mixture warmed, the so-called "plastic colophony" is obtained, m. p. 105—110°; after some time the mass, which contains absorbed alcohol, loses its plasticity, and after heating at 50—60° for a long time the m. p. rises to 115—120°. The aqueous solution of the sodium salt of γ-pinic acid absorbs a comparatively large quantity of ether. Colophony readily dissolves in petroleum, and when the solution is distilled the greater part of the solvent is removed; a small portion, however, remains with the colophony even when the latter is heated at 340°. This residue, m. p. 25° (approx.), frequently yields crystals of γ-abietic acid; it (the residue) amounts to about 40% of the weight of the colophony employed, is bright yellow in colour, and consists, apparently, of a compound of colophony with the higher hydrocarbons of petroleum. The light balsam mentioned previously by the author (A., 1914, i, 976), is a compound of colophony with hydrocarbons of high boiling point, and deposits crystals of abietic acid; the heavy balsam has more the properties of a resin oil and is free from hydrocarbons. If the calcium salt of γ-pinic acid is dissolved in petroleum and distilled, the residue remaining at 345° consists of a red-brown mass, which, when dissolved in twenty times its volume of petroleum, b. p. 275—300°, yields a brown solution; the latter forms a caoutchouc-like mass when cooled. Substances similar to vaseline are obtained when the mass is treated with benzene or nitrobenzene. The sodium salt of γ-pinic acid, when heated at 120° with 10 parts of petroleum, yields a colourless mass; this "solid petroleum" gradually gives off its petroleum. If petroleum, b. p. 170—250°, is employed, the mixture begins to thicken at 115° and "solid petroleum" separates. The latter burns with a smoky flame, and loses its petroleum when heated at a high temperature,

yielding a grey, viscous residue. The ammonium salt of the acid also yields a solid product when heated with petroleum and the mixture cooled. W. P. S.

Constitution of Anemonin. YASUHITO ASAHINA (*J. Pharm. Chim.*, 1915, [vii], **12**, 293—294; from *Yakugakuzasshi*, 1915, Feb. 1).—The author considers anemonin to be a dilactone of *cyclo*octadieneonedicarboxylic acid of the annexed constitution, since it is shown to contain two ethylenic linkings and on oxidation gives anemonic acid, which is identified as acetonediacetic acid. Further, anemonin gives a phenylhydrazone and reduces ammoniacal silver nitrate and Fehling's solutions, although the oxime and semicarbazone could not be obtained. The question as to whether anemonin is a dilactone or an anhydride was investigated by warming a solution to which half an equivalent of alkali hydroxide had been added. A neutral solution was obtained which became alkaline on further addition of alkali in the cold, but the alkalinity disappeared on warming. This behaviour is regarded as favouring the idea of a lactonic rather than an anhydride constitution, and is in accord with the above-suggested formula. G. F. M.



Loss of Weight of Musk in a Current of Dry Air. CHARLES B. BAZZONI (*J. Franklin Inst.*, 1915, **80**, 463—469).—Dry musk loses weight when exposed to a current of dried air, and when, after a period of about seven months, the loss of weight ceases the musk is no longer odorous. The odour, moreover, was not restored by exposure to moist air. 1·32245 mg. of dried musk lost 0·18941 mg. during the course of seven months, the average daily loss in milligrams during the consecutive months being 0·00318, 0·00135, 0·00087, 0·00035, 0·00025, 0·00017, and 0·00002. This gradual decrease in weight is regarded as being due solely to the evaporation of odorous volatile constituents. The weighings were made with a micro-balance consisting essentially of a quartz fibre rigidly supported in a horizontal position, to the free end of which a light pan containing the musk was attached, the whole being enclosed in a glass case; changes in flexure of the fibre due to changes in weight were measured by means of a microscope and micrometer screw. A sensibility of 0.00007 mg. was thus attained. G. F. M.

Condensation of Aromatic Hydroxyaldehydes with Diketohydrindene. SOSALE GARALAPURY SASTRY and BROJENDRA NATH GHOSH (T., 1915, **107**, 1442—1449).—The condensation of aromatic hydroxyaldehydes with 1-ketohydrindene in the presence of alkali (Perkin and Robinson, T., 1907, **91**, 1073) or of hydrochloric acid (Perkin, Robinson, and Turner, T., 1908, **93**, 1085) can be extended to diketohydrindene; this substance reacts with an *o*-hydroxy-aldehyde in the presence of an alkali hydroxide, giving an unsaturated ketonic derivative of the type $C_6H_4<^{CO}_{CO}>C{:}CH\cdot C_6H_4\cdot OH$, whilst under

the influence of hydrogen chloride the product is a ketoindenopyranol anhydrohydrochloride derivative of the type $\begin{matrix}C_6H_4\cdot C{:}OCl\\ CO{-}{-}C{:}CH\end{matrix}\!\!>\!C_6H_4$, which can be obtained from and converted into the former product by treatment with hydrogen chloride and aqueous alkali hydroxide respectively. The constitution of these products is confirmed by the results of Wislicenus and Kotzle (A., 1889, 1067) who have caused diketohydrindene to condense with other aldehydes. The high colour of these products obtained by the condensation of aromatic *o*-hydroxyaldehydes with diketohydrindene is referred to the orthoquinonoid structure represented above, which, however, differs slightly from the formulation $\begin{matrix}C_6H_4\cdot C{\cdot}OCl\\ CO{-}{-}C{\cdot}CH\end{matrix}\!\!\gg\!C_6H_4$ (Perkin, Robinson, and Turner, *loc. cit.*).

2′-Hydroxy-1 : 3-diketo-2-benzylidenehydrindene (*dibromide*, pale yellow needles, m. p. 122°), when treated with phenylhydrazine does not give a corresponding phenylhydrazone, but appears to undergo fission of the molecule.

Salicylaldehyde and diketohydrindene condense together in methyl-alcoholic solution containing hydrogen chloride, and there slowly separates at the ordinary temperature *4′-keto-2 : 3-indeno-1 : 4-benzopyranol anhydrohydrochloride*, $\begin{matrix}C_6H_4\cdot C{:}OCl\\ CO{-}{-}C{:}CH\end{matrix}\!\!>\!C_6H_4$, prisms, orange-red when moist, brown when dry, decomp. above 320°. This substance is also obtained when a methyl-alcoholic solution of 2′-hydroxy-1 : 3-diketo-2-benzylidenehydrindene is saturated with hydrogen chloride. When the above anhydrohydrochloride is treated in alcoholic solution with an aqueous solution of sodium acetate, a precipitate of *4′-keto-2 : 3-indeno-1 : 4-benzopyranol*, $\begin{matrix}C_6H_4\cdot C{:}O(OH)\\ CO{-}{-}C{=}{=}{=}CH\end{matrix}\!\!>\!C_6H_4$, brown needles of no definite m. p., is obtained. In hot aqueous-alcoholic solution, the anhydrohydrochloride is decomposed by sodium hydroxide with formation of 2-hydroxy-1 : 3-diketo-2-benzylidenehydrindene.

In alcoholic solution containing potassium hydroxide, the condensation of resorcylaldehyde and diketohydrindene yielded *2′ : 4′-dihydroxy-1 : 3-diketo-2-benzylidenehydrindene*,

$$C_6H_4\!<\!\begin{matrix}CO\\ CO\end{matrix}\!\!>\!C{:}CH\cdot C_6H_3(OH)_2,$$

brown prisms, decomp. at high temps.; the *acetyl* derivative, brown prisms, m. p. 235° (decomp.), gives a *dibromide*, brown needles unfused at 320°. When a solution of this dihydroxyhydrindene compound in methyl alcohol is treated with hydrogen chloride, further condensation occurs, with formation of *7-hydroxy-4′-keto-2 : 3-indeno-1 : 4-benzopyranol anhydrohydrochloride*, $\begin{matrix}C_6H_4\cdot C{:}OCl\\ CO{-}{-}C{=}CH\end{matrix}\!\!>\!C_6H_3\cdot OH$, bright red prisms decomp. at high temperatures, which is also obtainable directly by the condensation of resorcylaldehyde and diketohydrindene in methyl-alcoholic hydrogen chloride solution. On treatment with sodium acetate, the anhydrohydrochloride is converted into *7-hydroxy-*

4′-*keto*-2 : 3-*indeno*-1 : 4-*benzopyranol*, $\begin{matrix}C_6H_4\cdot C{:}O(OH)\\ |\quad\quad |\\ CO\text{---}C{=}{=}CH\end{matrix}>C_6H_3\cdot OH$, a dark brown, amorphous powder with a metallic lustre, whilst decomposition by sodium hydroxide in aqueous-alcoholic solution gives rise to 2′ : 4′-dihydroxy-1 : 3-diketo-2-benzylidenehydrindene.

Condensation of 2-naphthol-1-aldehyde with diketohydrindene in alcoholic solution in the presence of potassium hydroxide yields the *potassium* salt of 2′-*hydroxy*-1 : 3-*diketo*-2-*naphthylidenehydrindene*,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C{:}CH\cdot C_{10}H_6\cdot OH,$$

as a dark red crystalline mass; the free *hydroxy*-compound, liberated by acetic acid, forms dark red plates, m. p. 298° (decomp.), and gives a red coloration with ferric chloride; *sodium* salt, brown. In the presence of hydrogen chloride, condensation of the above naphtholaldehyde and diketohydrindene yields 4′-*keto*-2 : 3-*indeno*-1 : 4-*naphthapyranol anhydrohydrochloride*, $\begin{matrix}C_6H_4\cdot C{:}OCl\\ |\quad\quad |\\ CO\text{---}C{:}CH\end{matrix}>C_{10}H_6$, dark brown prisms decomp. at 130—150°, from which can be obtained in the usual manner 4′-*keto*-2 : 3-*indeno*-1 : 4-*naphthapyranol*, $\begin{matrix}C_6H_4\cdot C{:}O(OH)\\ |\quad\quad |\\ CO\text{---}C{=}{=}CH\end{matrix}>C_{10}H_6$, brown prisms, m. p. 125° (decomp.). D. F. T.

Conversion of the Natural Flavone Colouring Matters into Pyranol Dyes. Edwin Roy Watson, Kumud Behari Sen and Vishnu ram Medhi (T., 1915, **107**, 1477—1489. Compare Watson and Sen, T., 1914, **105**, 389).—It has been shown (*loc. cit.*) that 3 : 5 : 7-trihydroxy-2-*mp*-dihydroxyphenyl-4-ethyl-1 : 4-benzopyranol anhydrohydriodide, wrongly termed 3 : 5 : 7-trihydroxy-2-*mp*-dihydroxyphenyl-4-ethyl-1 : 4-benzopyran anhydrohydriodide in the previous communication, can be obtained by de-ethylation of the reaction product of quercetin pentaethyl ether and magnesium ethyl iodide. As dyes, this substance and the corresponding *anhydrohydrochloride* lack fastness.

3 : 5 : 7-*Triethoxy*-2-mp-*diethoxyphenyl*-4-*ethylbenzopyranol*

$$C_{15}H_5O(OEt)_5Et\cdot OH,$$

the free base corresponding with the above anhydrohydriodide and obtained by the action of aqueous ammonia on this salt is a colourless, viscous oil, which gives a *platinichloride*, $(C_{27}H_{35}O_6Cl)_2PtCl_4,2H_2O$, red needles, m. p. 197°. When the anhydrohydriodide is heated with aluminium chloride for an hour at 160°, partial de-ethylation occurs with formation of 3 : 5 : 7-*trihydroxy*-2-mp-*dihydroxyphenyl*-4-*ethyl*-1 : 4-*benzopyranol anhydrohydrochloride triethyl ether*,

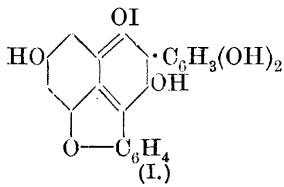
$$C_{15}H_5O(OEt)_3(OH)_2EtCl,H_2O,$$

an almost black powder which can also be produced from the anhydrohydriodide by the action of 33% sulphuric acid at 140°; this substance has tinctorial power equal to that of the analogous substances mentioned above, giving blue, greenish-blue, crimson, and navy blue shades respectively with alum, chrome, tin, and iron mordanted wool, the colours being fast to all agents. In the preparation of the triethyl ether as described, a small quantity of 3 : 5 : 7-*trihydroxy*-

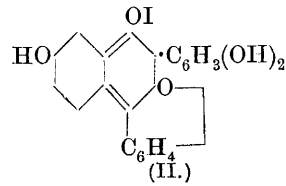
2-mp-*dihydroxyphenyl*-4-*ethyl*-1 : 4-*benzopyranol anhydrohydrochloride tetraethyl ether* was also obtained and was isolated as the *platinichloride*, $(C_{25}H_{31}O_6)_2PtCl_6,H_2O$, short scarlet prisms, m. p. 170—176° (decomp.).

The action of magnesium ethyl iodide on quercetin trimethyl ether gave 3 : 5 : 7-*trihydroxy*-2-mp-*dihydroxyphenyl*-4-*ethyl*-1 : 4-*benzopyranol anhydrohydriodide trimethyl ether*, $C_{15}H_5O(OMe)_3(OH)_2EtI,H_2O$, red needles, m. p. 163—165°, but the tinctorial power of this compound is small compared with that of the above triethyl ether, thus suggesting that the alkyloxy-groups occupy different positions in the two compounds. With magnesium phenyl bromide and quercetin pentaethyl ether the product after treatment with hydrochloric acid was 3 : 5 : 7-*triethoxy*-4-*phenyl*-2-mp-*diethoxyphenyl*-1 : 4-*benzopyranol anhydrohydrochloride*, $C_{15}H_5O(OEt)_5PhCl$, red needles, which, by boiling with hydriodic acid (D 1·7) was converted into 3 : 5 : 7-*trihydroxy*-4-*phenyl*-2-mp-*dihydroxyphenyl*-1 : 4-*benzopyranol anhydrohydriodide*, $C_{15}H_5O(OH)_5PhI$, deep red prisms, the corresponding free *base* being an unstable, amorphous, violet-coloured solid; as a dye, the salt was exceedingly fugitive.

3 : 5 : 7-*Triethoxy*-4-o-*methoxyphenyl*-2-mp-*diethoxyphenyl*-1 : 4-*benzopyranol anhydrohydrochloride*, $C_{15}H_5O(OEt)_5(C_6H_4\cdot OMe)Cl,HCl,H_2O$, obtained by the interaction of magnesium *o*-methoxyphenyl bromide and quercetin pentaethyl ether, was a crimson, crystalline solid which gave dyeings of greater fastness and deeper shades than the preceding compounds; it forms a *ferrichloride*, $C_{32}H_{37}O_7Cl,HFeCl_4$, red needles, m. p. 190°. The constitution of this compound is represented by either formula I or II. When this substance is heated with hydro-



(I.)



(II.)

chloric acid at 150—180°, de-ethylation occurs with production of a *substance*, $C_{21}H_{13}O_6Cl$, dark red needles with a blue reflex, which gives a green coloration with potassium hydroxide, and greenish-blue, green, dark blue and olive-green shades respectively with alum, chrome, tin, and iron mordants.

By the interaction of magnesium methyl iodide and *morin pentaethyl ether* (the latter substance, m. p. 112—114°, being obtained by exhaustive ethylation in the manner of Perkin, P., 1912, **28**, 328), in the presence of only a little ether, there was obtained 3 : 5 : 7-*trimethoxy*-2-op-*dimethoxyphenyl*-4-*methyl*-1 : 4-*benzopyranol anhydrohydriodide*, $C_{15}H_5O(OMe)_5MeI$, yellow needles, which on demethylation by boiling with hydriodic acid (D 1·7) was converted into 3 : 5 : 7-*trihydroxy*-2-op-*dihydroxyphenyl*-4-*methyl*-1 : 4-*benzopyranol anhydrohydriodide*, $C_{15}H_5O(OH)_5MeI$; this gives a crimson colour with potassium hydroxide and maroon, pink and salmon-coloured shades respectively with wool mordanted with chrome, tin, and iron.

Luteolin tetraethyl ether reacted readily with magnesium ethyl

iodide yielding 5 : 7-*diethoxy*-2-mp-*diethoxyphenyl*-4-*ethyl*-1 : 4-*benzopyranol anhydrohydriodide*, $C_{15}H_6O(OEt)_4EtI$, orange-coloured needles, m. p. 169—172°, from which the corresponding free *base*, $C_{15}H_6O(OEt)_4EtOH$, was obtained as colourless needles, m. p. 116—117°. When the tetraethyl ether anhydrohydriodide is de-ethylated by hydriodic acid the product is 5 : 7-*dihydroxy*-2-mp-*dihydroxyphenyl*-4-*ethyl*-1 : 4-*benzopyranol anhydrohydriodide*,

$$C_{15}H_6O(OH)_4EtI,H_2O,$$

which gives a violet coloration with potassium hydroxide and fast mauve, blue-black, maroon, and blue-black shades respectively with alum, chrome, tin, and iron mordants.

The interaction of apigenin trimethyl ether and magnesium ethyl iodide gave 5 : 7-*diethoxy*-2-p-*ethoxyphenyl*-4-*ethyl*-1 : 4-*benzopyranol anhydrohydriodide*, $C_{15}H_7O(OEt)_3EtI$, orange-coloured rhombs, m. p. 178—180° (*platinichloride*, $2C_{23}H_{27}O_4Cl,PtCl_4,2H_2O$, a bright red solid), which on de-ethylation by hydriodic acid was converted into 5 : 7-*dihydroxy*-2-p-*hydroxyphenyl*-4-*ethyl*-1 : 4-*benzopyranol anhydrohydriodide*, $C_{15}H_7O(OH)_3EtI,H_2O$, needles; this gave a crimson coloration with potassium hydroxide and brownish-orange to orange shades with various mordants.

Curves are given representing the absorption spectra of the above dyes, only one band being present throughout the whole class in the visible portion of the spectrum, although there are indications of a second band beginning near the ultra-violet end of the spectrum.

D. F. T.

The Diflavone Group. II. Derivatives of Diflavanone. Hugh Ryan and Pauline O'Neill (*Proc. Roy. Irish Acad.*, 1915, **32**, B, 167—184. Compare this vol., i, 707).—For the synthesis of diflavanone and diflavonol, considerable quantities of dihydroxydichalkone, or dibenzylidenediacetoresorcinol [4 : 6-dihydroxyphenylene distyryl diketone] were required. Whilst examining possible methods for preparing this compound, four isomerides were brought to light. The first of these, "α-dibenzylidenediresorcinol," was prepared by adding 50% sodium hydroxide to a solution of diacetylresorcinol and benzaldehyde in boiling alcohol (Eykman, Bergema, and Henrard, A., 1905, i, 359) and crystallises in long, orange-yellow, rhombic prisms, m. p. 204°. The next, the β-modification, was obtained by shaking a dilute aqueous-alkaline solution of diacetylresorcinol with benzaldehyde for about a month (*loc. cit.*) and crystallises in almost cubical, monoclinic, yellow prisms, m. p. 198—201°. If the latter process is prolonged to three months, the "γ-" form is formed, in pale yellow, equilateral triangular plates, m. p. 218°. A fourth isomeride, "δ-," is obtained by gently boiling the α-modification in solution in acetic acid saturated from time to time with hydrogen chloride. It forms yellow, diamond-shaped crystals, m. p. 205°. The β-modification gives a deep red coloration with alcoholic ferric chloride, the α-compound a fainter colour, the δ- a still paler colour, and the γ-isomeride practically no colour. The α-, β-, and δ-isomerides yield oily acetates which form the same tetrabromide of 4 : 6-dihydroxy-*m*-phenylene distyryl diketone diacetate (*ibid.*) on treatment with bromine, and then the same diflavone

with alcoholic potassium hydroxide. Since, by another synthesis, it has been shown that the β-compound is a true dihydroxyphenylene distyryl diketone (*ibid.*), the conclusion is drawn that the α-, β-, and δ-compounds are the three possible stereoisomerides of this. This is supported by the fact that the α-form changes into the β- when left with a trace of bromine in chloroform solution in the light. The γ-isomeride does not behave in the same way on acetylation and bromination, and is, therefore, a structural isomeride.

An attempt was made to prepare the dihydroxyphenylene distyryl diketone by heating *resorcinol dicinnamate*, $C_6H_4(CO_2{\cdot}CH{:}CHPh)_2$, with zinc or aluminium chloride, but without success. This ester was obtained by boiling together resorcinol, cinnamoyl chloride, and pyridine, and crystallised in prisms, m. p. 122—124°.

Derivatives of diflavanone can be prepared most readily by the condensation of diacetylresorcinol with aldehydes under the influence of alcoholic hydrogen chloride. Thus, with benzaldehyde the product is dibenzylidenediflavanone, m. p. 268° (Eykman, Bergema, and Henrard, *loc. cit.*), whilst piperonaldehyde yields *dipiperonylidene-3′ : 4′ : 3″ : 4″-dimethylenedioxydiflavanone*,

$$CH_2{:}O_2{:}C_6H_3{\cdot}CH{\cdot}O\rangle C_6H_2\langle O{-}CH{\cdot}C_6H_3{:}O_2{:}CH_2$$
$$CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}C{-}CO\rangle \qquad \langle CO{\cdot}C{:}CH{\cdot}C_6H_3{:}O_2{:}CH_2,$$

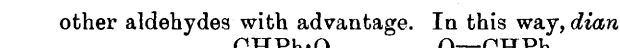
yellow prisms, m. p. 289°, almost insoluble in alcohol, mixed with the more soluble intermediate compound, *7-hydroxy-6-mp-methylenedioxycinnamoyl-3-piperonylidene-3′ : 4′-methylenedioxyflavanone*,

$$CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_2(OH)\langle \begin{matrix} O{-}CH{\cdot}C_6H_3{:}O_2{:}CH_2 \\ CO{\cdot}C{:}CH{\cdot}C_6H_3{:}O_2{:}CH_2 \end{matrix},$$

which crystallises in yellow prisms, m. p. 240—242°.

This condensation of hydroxy-ketones with aldehydes in the presence of alcoholic hydrogen chloride is also applicable to the monoflavone group, and is probably better than the usual process in alkaline media. Thus, gallacetophenone dimethyl ether [2-hydroxy-3 · 4-dimethoxyacetophenone] yields with benzaldehyde, *7 : 8-dimethoxy-3-benzylideneflavanone*, $C_6H_2(OMe)_2\langle \begin{matrix} O{-}CHPh \\ CO{\cdot}C{:}CHPh \end{matrix}$, colourless needles, m. p. 125—126°, and with anisaldehyde, *4′ : 7 : 8-trimethoxy-3-anisylideneflavanone*, $C_{26}H_{24}O_6$, nearly colourless prisms, m. p. 142—143°. With piperonaldehyde, the chief product is *7 : 8-dimethoxy-3′ : 4′-methylenedioxy-3-piperonylideneflavanone*, $C_{26}H_{20}O_8$, colourless needles, m. p. 184—186°, but some of the intermediate chalkone, namely *piperonylidenegallacetophenone dimethyl ether* [*2 : 3-dimethoxy-6-mp-methylenedioxycinnamoylphenol*], $OH{\cdot}C_6H_2(OMe)_2{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_3{:}O_2{:}CH_2$, may also be isolated, as it is soluble in dilute alkali hydroxide and more soluble in alcohol and chloroform than the main product. The chalkone is also formed by the alkaline condensation and crystallises in yellow prisms, m. p. 174—176°.

Eykman, Bergema, and Henrard (*loc. cit.*) prepared dibenzylidenediflavanone by the condensation of their α-dihydroxyphenylene distyryl diketone resorcinol with benzaldehyde in the presence of alcoholic hydrogen chloride. This method differs from the present one in that the intermediate chalkone is first isolated, but it may be applied to

other aldehydes with advantage. In this way, *dianisylidenediflavanone*,  pale yellow, rhombic crystals, m. p. 278—279°, and *dipiperonylidenediflavanone*, $C_{40}H_{26}O_8$, pale yellow prisms, m. p. 296°, have been prepared.

J. C. W.

Preparation of 2-Phenylquinoline-4-carboxylic Acid. KALLE & Co. (*Eng. Pat.*, 17725, July, 1914; from *J. Soc. Chem. Ind.*, 1915, **34**, 924).—2-Phenylquinoline-4-carboxylic acid is prepared by the condensation of isatin with acetophenone in aqueous-alkaline solution. Thus, isatin (16 kilos.), acetophenone (12 kilos.), and 33% potassium hydroxide (60 kilos.) are heated and stirred for eight hours on the water-bath, then diluted and filtered. Acetic acid is added as long as brownish-red flakes separate, and then the filtrate is treated with the calculated quantity of acetic acid in order to precipitate the 2-phenylquinoline-4-carboxylic acid.

J. C. W.

The Chromoisomerism of Acridonium Salts. A. HANTZSCH (*Ber.*, 1915, **48**, 1338—1340).—The author maintains his view of the chromoisomerism of acridonium salts and advances arguments against the suggestion of Kehrmann, Havas, and Grandmougin (A., 1913, i, 1241) that the variation in colour may be due to the formation of *meri*quinonoid salts.

D. F. T.

Diazonium Perhaloids. A. HANTZSCH (*Ber.*, 1915, **48**, 1344—1345).—The author opposes the formula $NRX{\cdot}NX_2$ suggested by Chattaway (T., 1915, **107**, 105) for the diazonium perhaloids and insists on their nature as ammonium perhaloids, this view being confirmed by the resemblance of the diazonium perbromide to *phenyltrimethylammonium tribromide*, golden-yellow scales, which is sparingly soluble in water with loss of bromine, and can be preserved almost unaltered over lime for two months.

D. F. T.

The Mechanism of the Coupling of Diazonium Salts with Amines, Phenols, and Phenolic Ethers. P. KARRER (*Ber.*, 1915, **48**, 1398—1406).—In an endeavour to prepare certain dialkylphenylenediamines by way of suitable aminoazo-compounds, the author has obtained results which suggest that in the coupling of a diazonium salt with an amine a primary addition of the salt occurs at the amino-group with formation of an ammonium derivative. This intermediate product then undergoes rearrangement into the azo-compound. An analogous intermediate formation of an oxonium compound is believed to occur in the condensation of a diazonium salt with a phenol or phenolic ether. If the nitrogen or oxygen atom is heavily laden with radicles, the affinity of the atom may be too nearly saturated for the formation of an additive compound, so that such substances as dibutylaniline and its *iso*amyl analogue cannot undergo condensation with diazosulphanilic acid without loss of an alkyl group, the final product being a monoalkylaminoazobenzenesulphonic acid,

$$NHR{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}SO_3H.$$

This view of the reaction is believed to accord satisfactorily with the results of Auwers and Michaelis (A., 1914, i, 744) Meyer, Irschick, and Schlösser (A., 1914, i, 882), and also with the observation that whereas *m*-chlorodimethylaniline reacts in the normal manner with a diazonium salt and with nitrous acid, *o*-chlorodimethylaniline fails to react at all with either reagent. According to the author's view of the action, the first effect with each reagent is an addition at the amino-group, and the process of addition is checked by steric hindrance in the case of the *o*-chloro-derivative. In the light of this explanation of the condensation of diazonium salts with amines or phenols, the intermediate compounds obtained with the latter by Dimroth and Hartmann (A., 1909, i, 66) should be of oxonium structure.

p-*Phenylenedipropyldiamine*, obtained by reduction of nitrosodipropylaniline with hyposulphite, forms, in addition to the normal sulphate, a *sulphate*, $2NH_2\cdot C_6H_4\cdot NPr_2,H_2SO_4$, colourless leaflets, which become red in the air.

Condensation of diazosulphanilic acid and dibutylaniline in aqueous acetic acid solution gives rise to red *butylaminoazobenzenesulphonic acid*, $C_4H_9\cdot NH\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot SO_3H$, which was separated as the *sodium* salt. When treated in aqueous solution with sodium hyposulphite, the sodium salt is reduced to *p*-butylaminoaniline. In a similar manner, iso-*amylaminoazobenzenesulphonic acid*, $C_5H_{11}\cdot NH\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot SO_3H$, and its *sodium* salt (orange-yellow leaflets) were obtained, the latter undergoing reduction with formation of p-iso*amylaminoaniline*, $NH_2\cdot C_6H_4\cdot NH\cdot C_5H_{11}$, leaflets, m. p. 31—32°; *hydrochloride*, leaflets.

D. F. T.

Polymorphic Phthalyl-halogen-substituted-phenyl- and -tolyl-hydrazides. Frederick Daniel Chattaway and Ernest Vonderwahl (T., 1915, **107**, 1503—1509).—The substitution of a halogen atom into the phthalyl-phenyl- and phthalyl-tolyl-hydrazides at the para-position, only causes the crystalline habit to become somewhat more slender, all the *p*-halogen derivatives crystallising in a yellow modification similar to the yellow modification of the parent compound. With the introduction of two halogen atoms into the 2- and 4-positions, the crystals become more elongated and hair-like, whilst a third halogen atom in the remaining ortho-position restores the original compact habit of the crystal. The meta-substituted derivatives, whether one position is substituted or both, crystallise in slender needles. The nature of the halogen is of little effect. Three cases of polymorphism were observed, the non-observance of other cases being probably due to excessive instability of one form or to unsuitable conditions.

Phthalyl-o-chlorophenylhydrazide, $C_6H_4<^{CO}_{CO}>N\cdot NH\cdot C_6H_4Cl$, forms compact, pale yellow plates, m. p. 221°. *Phthalyl-o-bromophenylhydrazide*, pale yellow plates, m. p. 212°. *Phthalyl-o-iodophenylhydrazide* crystallises in two polymorphic forms; very pale yellow, hair-like needles, and bright yellow, compact, rhombic plates, both m. p. 144—145°; both forms give identical deep yellow solutions. *Phthalyl-m-chlorophenylhydrazide*, pale yellow, hair-like prisms, m. p. 180°.

Phthalyl-m-*bromophenylhydrazide*, pale yellow, hair-like prisms, m. p. 208°. *Phthalyl*-m-*iodophenylhydrazide*, long, very slender, yellow prisms, m. p. 232°. The solubility of these meta-derivatives diminishes with increase in the atomic weight of the halogen whilst the colour deepens. *Phthalyl*-p-*iodophenylhydrazide*, forms long, bright yellow prisms, m. p. 193·5°; the *o*- and *m*-isomerides have already been described (Chattaway and Wünsch, T., 1911, **99**, 2260).

Phthalyl-2 : 6-*dibromophenylhydrazide* separates from toluene in pale yellow, microscopic prisms, m. p. 203°, which on suspension in toluene at the ordinary temperature are slowly replaced by large, colourless, hexagonal plates; when rapidly heated, this form shows signs of fusion near 190°, but simultaneously changes to the yellow form, which resolidifies and then melts at 203°. *Phthalyl*-3 : 5-*dibromophenylhydrazide*, faintly yellow, hair-like prisms, m. p. 268°. *Phthalyl*-3 : 4-*dibromophenylhydrazide*, pale yellow needles, m. p. 206°. *Phthalyl*-2 : 4-*dichlorophenylhydrazide*, pale yellow, hair-like prisms, m. p. 206°. *Phthalyl*-2 : 4-*dibromophenylhydrazide*, pale yellow, hair-like prisms, m. p. 224°.

Phthalyl-2-*chloro*-4-*bromophenylhydrazide*, very pale yellow, hair-like prisms, m. p. 210°. *Phthalyl*-4-*chloro*-2-*bromophenylhydrazide*, very pale yellow, hair-like prisms, m. p. 211°.

2 : 4 : 6-Tribromophenylhydrazine was obtained by diazotising a solution of tribromoaniline in solution in a mixture of concentrated sulphuric and glacial acetic acids with aqueous sodium nitrite, and reducing the resulting solution with an acid solution of stannous chloride (compare Neufeld, A., 1889, 251). It readily undergoes atmospheric oxidation, with formation of tribromobenzene and nitrogen (compare Chattaway, T., 1907, **91**, 1323; 1908, **93**, 270).

Phthalyl-2 : 4 : 6-*tribromophenylhydrazide*, forms pale yellow, short compact prisms, m. p. 205°.

Phthalyl-2 : 4 : 6-*trichlorophenylhydrazide*, stout, almost colourless prisms, m. p. 191°.

Phthalyl-2 : 6-*dichloro*-4-*bromophenylhydrazide*, pale yellow, compact, rhombic plates, m. p. 188°.

Phthalyl-2 : 4-*dichloro*-6-*bromophenylhydrazide*, pale yellow, short, stout prisms, terminated by pyramids, m. p. 193°.

Phthalyl-4-*chloro*-2 : 6-*dibromophenylhydrazide*, very pale yellow, short, stout prisms, m. p. 217°.

Phthalyl-6-*chloro*-2 : 4-*dibromophenylhydrazide*, very pale yellow, compact, stout, irregular plates, m. p. 195°.

Phthalyl-3 : 5-*dibromo*-o-*tolylhydrazide*, forms long, colourless, very slender prisms, m. p. 236°.

Phthalyl-3 : 5-*dibromo*-p-*tolylhydrazide*, separates from hot toluene or glacial acetic acid in very pale yellow, long needles, which, when left in contact with acetic acid at the ordinary temperature, soon change into pale yellow, compact crystals, apparently very short, stout prisms; the m. p. of both forms is 196°.

The trihalogen-substituted hydrazines other than 2 : 4 : 6-tribromophenylhydrazine, of which derivatives are described above, were prepared in a similar manner to 2 : 4 : 6-tribromophenylhydrazine, and will be described later. D. F. T.

The Activity, during the Biochemical Synthesis of β-Alkyl Glucosides by β-Glucosidase, of the Other Ferments Accompanying it in Emulsin. EM. BOURQUELOT and A. AUBRY (*Compt. rend.*, 1915, **161**, 463—466; *J. Pharm. Chim.*, 1915, [vi], **12**, 305—314).

Of the enzymes occurring along with β-glucosidase in emulsin, lactase and β-galactosidase do not exert any influence on the synthesis of alkyl glucosides from dextrose. Gentiobiase and cellase exert their own synthesising action, tending to produce gentiobiose and cellose. The formation of these sugars is found to be much greater as the proportion of dextrose to water in the mixture increases and as the alcohol becomes less concentrated. The addition of acetone to the aqueous sugar solution does not affect the amount of these two hexobioses formed relative to the water-sugar volume. In order to obtain the best yield of alkylglucoside when working with emulsion the aqueous sugar solution should not contain more than 15—20% of dextrose. W. G.

Physiological Chemistry.

A Respiratory Chamber for Small Animals. A. C. KOLLS and A. S. LOEVENHART (*Amer. J. Physiol.*, 1915, **39**, 67—76).—The paper is devoted entirely to a full description, with figures, of the apparatus. Results will be presented later. W. D. H.

The Mechanism Adapting the Oxygen Capacity of the Blood to the Requirements of the Tissues. H. C. DALLWIG, A. C. KOLLS, and A. S. LOEVENHART (*Amer. J. Physiol.*, 1915, **39**, 77—108).—Decrease in oxygen tension to 14% of an atmosphere stimulates the bone marrow in rabbits, rats, and dogs. The consequent increase of red corpuscles and hæmoglobin is marked in five to seven days, but the maximum occurs later. The increase is absolute, and in rats it may reach 43%. The effect is more marked when the oxygen pressure is reduced to 10% of an atmosphere, and is still seen when 6% is employed. Carbon dioxide also stimulates the bone marrow to a certain small extent. W. D. H.

The Gases of the Blood During Hibernation in the Woodchuck (Marmota Monax). ANDREW T. RASMUSSEN (*Amer. J. Physiol.*, 1915, **39**, 20—30).—The amount of carbon dioxide in the blood of the woodchuck is always high; it increases during hibernation, and falls on waking. There is also more oxygen in the arterial blood just preceding and during torpidity than at other times. The difference between arterial and venous blood is greater during hibernation, especially in the carbon dioxide content. W. D. H.

The Influence of Nutrition and Exercise on the Blood-sugar Content. W. von Moraczewski (*Biochem. Zeitsch.*, 1915, **71**, 268—288).—The effect of ingestion of carbohydrates by individuals on insufficient diet is to cause a transient rise of the blood-sugar; proteins, under similar conditions, cause a smaller but more lasting rise. The effect on individuals on a diet more than sufficient for bodily needs is as follows: carbohydrates are without action, whereas proteins and fats cause an insignificant but lasting rise. The influence exerted by exercise on the blood-sugar depends on the diet; the rise is somewhat greater on a diet of carbohydrates and gelatin than on a meat and fat diet. In the case of diabetic individuals, the rise of the blood-sugar produced by diet and exercise is smaller; on all diets, muscular exercise causes an increase in the blood-sugar. The tolerance to sugars is increased by muscular exercise, and even in the case of diabetics there is a diminution of the excretion of sugar after muscular work, in spite of the rise of the blood-sugar. S. B. S.

The Origin of the Proteolytic Enzymes of the Blood. Le Roy H. Sloan (*Amer. J. Physiol.*, 1915, **39**, 9—19).—The proteolytic action of the serum rises in pregnancy. Normal serum has a weak, non-specific, proteolytic action, and the enzyme during pregnancy is not specific for placental protein. Many pathological conditions produce the same effect as pregnancy. The Abderhalden test is therefore quantitative, not qualitative. W. D. H.

Blood-counts in Frog, Turtle, and Twelve Mammals. J. J. Wells and J. E. Sutton, jun. (*Amer. J. Physiol.*, 1915, **39**, 31—36).—Statistical. Enormous variations occur from less than a million red corpuscles per cubic millimetre in cold-blooded animals to more than twenty millions in goats. Details of the white corpuscles are also given, but no differential counts were attempted. W. D. H.

The Osmotic Equilibrium between Blood, Milk, and Bile. F. H. van der Laan (*Biochem. Zeitsch.*, 1915, **71**, 289—305. Compare this vol., i, 622).—Milk and bile have the same osmotic concentration as the blood from which they are secreted. The normal depression of freezing point for ox-blood is 0·53—0·57°. The freezing point is independent of the temporary state of nutrition of the animal, and even starvation for several days leads to no change in the freezing point of the blood or milk. By dilution of the contents of the small intestine, or by administration of sodium sulphate, the depression of the freezing point of the blood can be altered; even under these conditions, the osmotic equilibrium between blood and milk can be maintained. The estimation of the freezing point of milk is the most certain method for detection of the addition of water, and any milk which freezes above −0·53° must be regarded as adulterated. S. B. S.

The Physiology of Clot Formation. The Influence of Acids and Alkalis. Action of Protein Precipitants. A Theory of Clot Formation. E. Herzfeld and R. Klinger (*Biochem. Zeitsch.*, 1915, **71**, 391—405).—The optimal condition for the formation of

thrombin is the presence of a neutral medium, or one slightly alkaline to sodium hydrogen carbonate; the formation is inhibited by acids in very small concentrations. On the other hand, acids accelerate the thrombin action (precipitation of fibrin), whereas alkalis exert an inhibitory action. Thrombin action is also accelerated by various protein precipitants. Attempts were made to apply Herzfeld's theory of the solubility and precipitation of proteins to the process of clotting, and it was shown that the solubility of fibrinogen is affected by certain protein degradation products, especially fibrin peptone (compare this vol., i, 1019).

S. B. S.

Physiology of the Stomach. XXVII. The Mechanism of the Regurgitation of Duodenal Contents into the Stomach. CLARENCE J. HICKS, jun., and JOHN W. VISHER (*Amer. J. Physiol.*, 1915, **39**, 1—8).—Hydrochloric acid (150 c.c. of 0·5%) causes regurgitation when left in dogs' stomachs for fifteen to thirty minutes. The same is frequently noticed in man. From similar observations on cats, it is concluded that this is not due to antiperistalsis, but to "segmentation movements" of the duodenum.

W. D. H.

Physiology of the Stomach. XXIX. The Gastric Hunger Contractions of the Normal and Decerebrate Guinea Pig. JESSIE L. KING and HELENE CONNET (*Amer. J. Physiol.*, 1915, **39**, 123—130).—Hunger contractions appear in the guinea-pig four to five hours after feeding, while the stomach is well filled. Water, 0·5% hydrochloric acid, and other substances which usually inhibit these contractions give negative results. After eating, the vigorous movements continue for half an hour, and then merge into those of the mild peristaltic type. Hunger movements appear to be vigorous peristaltic contractions. After decerebration, the stomach is in a hypertonic condition, owing, presumably, to the absence of inhibitory impulses from the cortex. W. D. H.

The Utilisation of Blood for Human Diet, and the Behaviour of Formaldehyde in the Organism. E. SALKOWSKI (*Biochem. Zeitsch.*, 1915, **71**, 365—390).—Ox-blood contains nearly the same amount of protein as fat-free meat, and has nearly the same nutritional value. Experiments are described on the methods of preserving the material by the addition of antiseptics. It was found that the coagulated proteins could be preserved in chloroform water and in $\frac{1}{2}$% formaldehyde solution. The effect of formaldehyde on the system was investigated, and it was found that dogs could tolerate 0·6—1 gram daily in their food, of which about 0·6% was excreted unchanged in the urine. It is contended that the toxicity of this substance has been over-estimated. Attention is directed to the fact that there exists in urine a substance which gives with iodine and sodium hydroxide the iodoform reaction, and of which the nature is unknown. S. B. S.

The Influence of the Depressor Nerve on Suprarenal Secretion. A. N. Richards and Wilson G. Wood (*Amer. J. Physiol.*, 1915, **39**, 54—66).—The processes in the suprarenal gland responsible for the discharge of adrenaline are subject to reflex inhibition via the depressor nerve. W. D. H.

The Stimulation of the Hypophysis in Dogs. Robert W. Keeton and Frank C. Becht (*Amer. J. Physiol.*, 1915, **39**, 109—122). —If asphyxia is avoided, ether anæsthesia causes no marked rise in the reducing power of the blood; after one to three hours it may fall. Stimulation of the hypophysis (pituitary) then increases the reducing power, but this does not occur if the splanchnic nerves are cut. W. D. H.

A Labile Form of Proteins, and its Relationship to Living Protoplasm. Oskar Loew (*Biochem. Zeitsch.*, 1915, **71**, 306—320). —A labile form of protein exists in many cells, generally in the cell-juice, but sometimes also in the protoplasm. This substance is distinguished from ordinary proteins by the fact that it is separated from solution by the addition of ammonia and organic bases, and then rapidly undergoes a change, and is converted into a more stable compound. The action of the alkali is not a mere neutralisation. The more reactive bases cause, as a rule, the separation of numerous small granules, whereas weaker bases, such as caffeine and antipyrine, act in quite a different manner. In the presence of these bases, cell life can remain intact for several days, and the protein can retain its labile form. Very small drops of the substance separate at first, and these combine gradually to larger refractive drops, which can reach the diameter of 30 μ, that is, about half the diameter of the cell. The changes produced on these objects ("proteosomes") can be readily followed by the microscope. They coagulate by the expulsion of water, forming either a hollow sphere or a sphere containing varying numbers of cavities, or an amorphous mass without definite form. Such a change can be produced by hydrogen cyanide, hydroxylamine, or hydrazine. Ammonia produces a solid structure without, as a rule, cavities. The labile protein behaves towards dyes like the living protoplasm, whilst the coagulated "proteosomes" behave like dead protoplasm. It is claimed that there is an intimate relationship between the stored labile protein and the organised labile protein or protoplasm. S. B. S.

The Colloidal Nitrogen in Normal and Pathological Urine. Gh. Dumitrescu (*Chem Zentr.*, 1915, ii, 34—35; from *Bul. Soc. Ştiinte Bucareşti*, 1915, **17**, 13—22).—The colloidal nitrogenous matter was precipitated with zinc chloride, and the organic matter in the precipitate was destroyed in the usual manner. After neutralisation with sodium hydroxide, the nitrogen was estimated by hypobromite. By this method, it was found that the relationship of colloidal to total nitrogen could rise to 2·57 on a meat diet, whereas it was less on a mixed diet, and still less on a milk and

vegetable diet. In cancer there was a tendency for the number to rise, according to the severity of the disease. The same was true in diabetic cases, but here the amount of dextrose in the absence of acidosis was without influence on the number. This was also influenced by diseases of the liver and kidneys, but not in cases when the urine contains pus. S. B. S.

Acidosis and its Regulation in the Human Body. A. Begun, R. Herrmann, and E. Münzer (*Biochem. Zeitsch.*, 1915, **71**, 255—267).—From experiments and clinical observations, it is found that acids in the system, whether introduced in experiment or resulting from a pathological condition, are eliminated as ammonium salts in the urine. No change in the tension of carbon dioxide in the venous blood is produced thereby, so that this factor cannot be regarded as a measure of acidosis. Diminished carbon dioxide tension cannot by itself, without taking into account other factors, be regarded as a measure of acidosis. The carbon dioxide tension of the blood does, however, sink after prolonged acidosis, but this is due to the impoverishment of the blood in substances capable of combining with carbon dioxide, or perhaps to an alteration in the tissues; whether alteration in the respiration is involved at the same time cannot be decided without further experiments. The tension of the carbon dioxide of the venous blood standing in equilibrium with the alveolar air is in the first instance dependent on the carbon dioxide content of the blood, and is apparently a function of the capacity of the blood for binding this gas. The carbon dioxide tension of the blood can sink also without any acidosis. S. B. S.

The Immediate Effects of the Inhalation of Chlorine. Sir Edward A. Schäfer (*Brit. Med. J.*, 1915, ii, 245—247).—In anæsthetised cats and dogs, injection of chlorine dissolved in Ringer's solution directly into the blood-stream is not followed by serious results, but inhalation is always followed by toxic symptoms, the most marked of which is cessation of breathing, which follows exaggerated efforts to respire, and recovery after two successive inhalations of 1 part of chlorine to 100 of air is not usually obtainable; the blood pressure, after a slight rise, falls. There appears to be no bronchial constriction, but the chief cause of the symptoms is circulatory failure through the lungs, which amounts in some cases to complete stasis. There is also much œdema in the pulmonary tissue. The bodies of the animals do not smell of chlorine. The heart beats for some time after the respiration stops. Nothing special was noted in other organs. Tracings and drawings of microscopic specimens of the lungs are given.
W. D. H.

The Influence of Oil of Chenopodium on Intestinal Contractility. William Salant and C. W. Mitchell (*Amer. J. Physiol.*, 1915, **39**, 37—53).—Oil of chenopodium in dilution of 1:5000 and 1:10,000 markedly lessens the tone and contractions of intestinal

loops, especially of the colon; in dogs this may be preceded by a rise of tone. Recovery occurs in pure Locke's solution. Large doses are necessary to inhibit peristalsis in intact rabbits if intravenous injection is used. Nerve-endings as well as muscle fibres are attacked, the latter being the more resistant. The action of the oil is not antagonised by caffeine, pilocarpine, or barium chloride. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Schumann Rays as an Agent for the Sterilisation of Liquids. W. T. Bovie (*Bot. Gaz.*, 1915, **60**, 144—148).—It is shown that a hydrogen discharge tube as described by Billon-Daguerre is not an efficient source of light for photo-sterilisation. An apparatus similar to the one referred to is described in which the exposure was much longer, whilst the volume of liquid exposed at any one time was much less. Although the numbers of bacteria were greatly reduced, sterilisation was not complete.

N. H. J. M.

Fermentation of Carbohydrates by Living and Killed Yeast Cells. Hans Euler (*Bied. Zentr.*, 1915, **44**, 419—421; from *Zeitsch. Gährungsphysiol.*, 1914, **5**, 1).—Yeast was dried in a vacuum (3—5 mm. mercury pressure), at a temperature of 25° which was gradually raised to 60°, and treated with alcohol previously distilled over lime and calcium. On adding toluene (2 c.c.) to an emulsion of 1 gram of the dry yeast in 25 c.c. of 8% dextrose solution, it was found that the fermenting power was reduced 60% to 125%. It was found that about 5% of the yeast cells remained uninjured, and when examined microscopically, with and without dyes, behaved the same as living cells. The cells, termed "zymatic cells," retain the function of fermentation catalysis, whilst the power of growth is lost.

N. H. J. M.

Fixation of Elementary Nitrogen by Yeasts and Moulds. Alexander Kossowicz (*Bied. Zentr.*, 1915, **44**, 425—427; from *Zeitsch. Gärungsphysiol.*, 1914, **4**, 25—32).—The results of experiments with yeast and several moulds showed that very little nitrogen is necessary to obtain growth and that the combined nitrogen in the air was sufficient. It is therefore considered doubtful whether any yeasts and moulds have the power of utilising elementary nitrogen.

N. H. J. M.

Effect of Some Tervalent and Quadrivalent Cations on Permeability. W. J. V. Osterhout (*Bot. Gaz.*, 1915, **59**, 464—473).—It is shown that all the tervalent cations investigated.

namely, lanthanum, cerium, yttrium, iron, and aluminium, and the quadrivalent cation thorium, can decrease permeability.

N. H. J. M.

Constant Changes in the Forms of Antagonism Curves. W. J. V. Osterhout (*Jahrb. wiss. Botan.*, 1914, **54**, 645—650).—Experiments are described in which sections of *Laminaria* were kept in solutions containing sodium chloride (100—0 mols.) and calcium chloride (0—100 mols.) for varying periods, the antagonistic action being measured by the electrical method. It is shown that the curves for the different relations of sodium and calcium chlorides change in form as the experiment proceeds. After immersion for half an hour, the resistance in pure sodium chloride fell from 100% to 85%, whilst in the pure calcium chloride there was a rise from 100% to 138%. In a solution containing 80 mols. of NaCl to 20 mols. of $CaCl_2$ the resistance rose from 100% to 126%. After one hour, the resistance in pure sodium chloride fell to 60%, whilst in pure calcium chloride it rose to 140%. In sodium chloride and calcium chloride (38:62) the resistance rose to 147%. After seventeen hours, the resistance in pure sodium chloride fell to 10% (death point), and in pure calcium chloride to 41%, whilst the greatest resistance, 119%, was in sodium chloride and calcium chloride, 80:20. Curves are also given for twenty-four, forty-two, and sixty-two hours.

At first sodium chloride increases the permeability of the tissues, whilst calcium chloride has the opposite effect. Later, calcium chloride increases permeability; the process by which this is effected is, however, probably different from that with sodium chloride.

N. H. J. M.

Absorption of Ions by Living and Dead Roots. H. V. Johnson (*Amer. J. Botan.*, 1915, **2**, 250—254).—When live beet roots were placed in solutions of calcium chloride, it was found that 41·31% of the calcium and 43·74% of the chlorine were removed from the solution. Dead roots of the same plant removed 44% of calcium and only 26·25% of the chlorine. Similar results were obtained with carrots. In experiments with sweet maize, the dead roots took up somewhat more calcium than chlorine.

The presence of dead cells has, therefore, in some cases a marked effect on the results, and it is desirable to avoid toxic solutions, which may kill some of the cells while the experiment is going on.

In Meurer's experiments (*Jahrb. wiss. Bot.*, 1909, **46**, 503), the outer layers of beet and carrots were cut away with a knife, so that the solutions had to penetrate a layer of dead cells before reaching the living tissue.

N. H. J. M.

The Organic Diet of Green Flowering Plants. Th. Bokorny (*Biochem. Zeitsch.*, 1915, **71**, 321—364).—A large number of experiments are described in which comparisons are made between the growth of plants nurtured on the one hand with the ordinary inorganic media, and on the other with the same media and the addition of organic substances. Beans, cabbages, *Spirogyra*,

cucumbers, and other plants were employed, and the organic substances used were methyl alcohol, glycerol, and methylal. In many cases it could be shown that the addition of organic substances increased the growth of the plant. S. B. S.

Evidence for the General Distribution of Oxydases in Plants. G. B. Reed (*Bot. Gaz.*, 1915, **59**, 407—409).—It is shown that algæ as a class possess a ferment capable of activating the oxidation of a limited number of compounds, and that the ferment is specific in its action.

Oxydases are of general occurrence among the algæ, and the results, together with observations on acid tissues, indicate that the oxydases are universally distributed in living plants.

N. H. J. M.

The Localisation of Acids and Sugars in Fleshy Fruits. E. Demoussy (*Compt. rend.*, 1915, **161**, 443—445).—Various species of fleshy fruit, both fully and partly ripe, have been subjected to gradually increasing pressure and the juices expressed, fractionally collected, the successive fractions being separately analysed for acidity and sugar content. There was often marked difference in the acidity of the various fractions, the last fraction in the case of plums being seven times more acid than the first. These variations were also marked for apricots and grapes, slight for peaches, and non-existent in the case of strawberries, melons, and apples. With cherries and tomatoes the acidity diminished as the pressure increased. Of the sugars, the reducing sugars varied in the same sense as the acidity, but to a lesser extent, whilst the sucrose content varied in an opposite direction. Similar results were obtained by plasmolysis in a strongly hypertonic solution in place of pressure. The author considers that those cells which are less resistant to pressure or the walls of which are more permeable, and in consequence empty first, contain a juice having a different chemical composition from those which empty last. There is localisation, but the direction of variation is not always the same for all fruits. These results are discussed from the point of view of the osmotic pressure in the cells, and they afford an apparent explanation of the increase in acidity of fruits on cooking, the more acid cells not being broken in the process of eating in the raw, ripe state. W. G.

Influence of the Pyrrole Nucleus on the Formation of Chlorophyll. Gino Pollacci and Bernardo Oddo (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 37—39).—The authors have investigated the influence of *magnesium pyrrole-2-carboxylate*,

$$(C_4H_4N\cdot CO_2)_2Mg,2H_2O,$$

on the production of chlorophyll in *Zea mais* (compare Oddo, A., 1914, i, 1176; Mameli, this vol., i, 631, 633). The plant grows well in solutions containing 0·05% of this salt. The seeds were then germinated in two solutions containing calcium and potassium nitrates, ammonium sulphate, and potassium dihydrogen phos-

tained in the body on the one hand, and the amounts of phosphorus ingested, the amounts of protein ingested, or the body-weights of the lambs on the other.

Variations in the amount of digestible protein consumed, from 1·56 to 3·19 lbs. per 1000 lbs. of live weight per day, have no significant effect on the forms of phosphorus in the fæces, the total phosphorus in the urine, or the total phosphorus stored in the body, expressed in percentage of the total phosphorus ingested.

N. H. J. M.

Antagonism between Anions as Affecting Barley Yields on a Clay-adobe Soil. CHARLES B. LIPMAN and W. F. GERICKE (*J. Agric. Research*, 1915, **4**, 201—218).—Pot experiments in which two crops of barley were grown, with an interval of three months, in soil to which different amounts of sodium chloride, sulphate, and carbonate, respectively, were added; also experiments on antagonism between sodium chloride and sulphate, sodium chloride and carbonate, sodium carbonate and sulphate, and calcium sulphate and sodium sulphate.

In the control experiment, the yield of the second crop was much greater than that of the first, owing to improvement in the soil from alternate wetting and drying and the thorough drying during the period of rest. Small amounts (0·1%) of sodium chloride and of sodium sulphate acted as stimulants on the first crop and as poisons in the second crop, whilst sodium carbonate was not toxic at all, but showed stimulation in concentrations up to 0·3% of the dry weight of the soil.

Antagonism was shown between sodium chloride and sulphate and between sodium chloride and carbonate in the second crop, but not in the first. In the case of sodium carbonate and sulphate, a slight antagonism was shown in the first crop. Both the first and the second crops showed a marked antagonism between sodium sulphate and calcium sulphate.

The pots received insufficient water to give drainage, and practically the whole of the sodium chloride and sulphate could be recovered at the end of the experiments. In the case of sodium carbonate, the highest amount recovered was 25%. N. H. J. M.

Assimilation of Colloidal Iron by Rice. P. L. GILE and J. O. CARRERO (*J. Agric. Research*, 1914, **3**, 205—210).—Water culture experiments with rice in which colloidal iron and ferric chloride were compared as sources of iron. In order to prevent precipitation of the colloidal iron, the nutrient solution was put into one flask and the iron into a second flask, the plants being grown with part of their roots in each flask. The colloidal iron employed was the ordinary dialysed iron, and contained some chlorine.

The plants supplied with colloidal iron assimilated a small amount of iron, probably soluble iron, which must be assumed to be present. The conclusion is drawn that colloidal iron was not assimilated, and that if roots secrete acids at all there was at any rate no secretion in the unbalanced solution employed. In the

extracts of *Boletus edulis*, but more particularly those which yielded amino-acids. The dried fungus has now been extracted with ether, alcohol, and then water, according to Reuter's method, and the dried residue after these extractions has been examined for amino-glucosides by the method of Kotake and Sera. After hydrolysing with sulphuric acid, however, no glucosamine could be detected, but, using concentrated hydrochloric acid as the agent, the same amount of the hydrochloride was isolated as Reuter obtained. The conclusion is drawn that the glucosamine in *Boletus edulis* is pre-existent as a glucoprotein and not as a glucoside, and that it is only under special conditions that glucosamine is a cleavage product. Thus a glucoprotein might be hydrolysed to a sugar and an amide, or an amino-sugar and an acid, according to the scheme $\text{:CH·NH·CO·CH:} \longrightarrow \text{:CH·OH} + \text{NH}_2\text{·CO·CH:}$ or $\text{:CH·NH}_2 + \text{CO}_2\text{H·CH:}$. J. C. W.

The Root Bark of Calotropis gigantea. Ernest George Hill and Annoda Prasad Sirkar (T., 1915, **107**, 1437—1442).—By extracting large quantities of the root bark of *Calotropis gigantea* with boiling alcohol, the authors have obtained an oily substance, a white solid, a substance somewhat resembling gutta-percha, and a small quantity of a yellow bitter principle.

The white solid was separated by fractional crystallisation from hot alcohol into a substance, $C_{35}H_{56}O_3$, nodular crystals, m. p. 140°, $[\alpha]_D^{23}$ +128° (in ether), and a substance, $C_{43}H_{70}O_3$, needle crystals, m. p. 210°, $[\alpha]_D^{23}$ +119°. The former substance on hydrolysis with potassium hydroxide yielded potassium *iso*valerate and an alcohol, *mudarol*, $C_{30}H_{48}O_2$, hexagonal plates, m. p. 176° (*acetate*, needles, m. p. 195—196°), and was therefore identified as *mudaryl* iso*valerate*, $C_{30}H_{47}O\text{·}CO_2\text{·}C_4H_9$; the alcohol was oxidised by a solution of chromic acid in acetic acid solution to *mudaric* acid, $C_{30}H_{45}O_3H$, an amorphous solid, m. p. 225°; the *silver* salt was a very pale green, amorphous solid. The solid, m. p. 210°, on hydrolysis gave *iso*valeric acid and *akundarol*, a monohydric primary alcohol, $C_{38}H_{61}O\text{·}OH$, needles, m. p. 215° (*acetate*, needles, m. p. 222°), and was thus identified as *akundaryl* iso*valerate*, $C_{38}H_{61}O\text{·}CO_2\text{·}C_4H_9$; when oxidised with chromic acid, the alcohol was converted into *akundaric* acid, $C_{38}H_{59}O_3H$; *silver* salt, an amorphous, pale green solid. These two alcohols and their *iso*valerates give colour reactions similar to those of cholesterol and phytosterol.

The third product obtained by the extraction of the root-bark resembled gutta-percha only when warmed; its composition approximated to the formula $C_{34}H_{47}O_{12}N$. No caoutchouc whatever could be detected in the plant. The yellow bitter principle gave the usual precipitation reactions for alkaloids, but it was not possible to isolate any alkaloid in a pure condition.

These results are at considerable variance with those obtained by Warden and Waddel (*Pharm. J.*, 1885, 165), who reported a "caoutchouc" as being present in the plant; the "madar-alban"

of these investigators is probably identical with the crude mixture of mudaryl and akundaryl *iso*valerates described above.

D. F. T.

Plant Chemistry. P. Q. Keegan (*Chem. News*, 1915, **112**, 203—205).—Analyses, organic and inorganic, of canary grass, purple loosestrife, heather, and ragwort. N. H. J. M.

Application of the Biochemical Method to the Examination of the Stone-kernels of the Cherry Laurel. Marc Bridel (*J. Pharm. Chim.*, 1915, [vii], **12**, 249—252).—The stones of the cherry laurel fruit (*Prunus Laurocerasus*) yield about 55% of their weight of kernels, and the latter have a composition very similar to that of bitter almonds. The kernels contain 4·0% of amygdalin (about 19% more than is present in bitter almonds) and 3·0% of sucrose. The leaves of the cherry laurel contain a cyanogenetic glucoside, a derivative of racemic phenylglycollic acid, whilst that present in the kernels is a derivative of *d*-phenylglycollic acid. W. P. S.

Chrysanthemum cinerariæfolium, Trev. P. Siedler (*Ber. Deut. pharm. Ges.*, 1915, **25**, 287—302).—Directions are given for the cultivation of this plant, the dried, powdered flowers of which are largely used as an insect powder. The insecticidal principle is shown to be present mainly in the discoid flowerets, and is not removed by distillation with steam. The pasty mass ultimately obtained in a yield of 0·067% by distilling the flowers with steam has a pronounced aromatic odour, and gives indications of the presence of acids, aldehydes, ketones, phenols, esters, and hydrocarbons, but in almost every instance the amount of substance isolated has been too small to admit of identification. One of the acids obtained is regarded as palmitic acid on the evidence of its m. p., 62°; a hydrocarbon, $C_{14}H_{30}$, slender needles, m. p. 54—56°, has also been isolated. C. S.

Chemistry of the Higher Fungi. Julius Zellner (*Monatsh.*, 1915, **36**, 611—632).—Analyses of different extracts (light petroleum, ether, alcohol, and water) of *Lactarius scrobiculatus*, *Hydnum ferrugineum*, *Hydnum imbricatum*, and *Polyporus applanatus*.

From the alcoholic extract of *Hydnum ferrugineum* there were obtained thelephoric acid (Zopf), mannitol, dextrose, and two benzoic esters which when hydrolysed yielded resinotannols. *Hydnoresinotannol benzoate* (*A*), $C_{33}H_{26}O_8$, forms microscopic (? rhombic) crystals, sparingly soluble in hot alcohol, m. p. 272° (uncorr.), with decomposition. The *acetyl* derivative, m. p. 276°, resembles the parent substance. *Hydnoresinotannol benzoate* (*B*), $C_{30}H_{20}O_7$ or $C_{30}H_{22}O_7$, dissolves readily in hot alcohol; m. p. 251—252° (decomp. uncorr.). The *acetyl* derivative,

$$C_{30}H_{18}O_7(CO\cdot CH_3)_2 \text{ or } C_{30}H_{20}O_7(CO\cdot CH_3)_2,$$

forms microscopic groups of fine needles and prisms, m. p. 182° (uncorr.). A *nitro*-compound, m. p. 227° (uncorr.), with decomposition, was also prepared. N. H. J. M.

The Carbohydrates of Fir-wood. Erik Häggland (*Biochem. Zeitsch.*, 1915, **70**, 416—425).—The carbohydrates yield on hydrolysis chiefly xylose and mannose, together with some lævulose and galactose. Dextrose cannot be detected. On hydrolysis of the wood with dilute acids at higher temperatures, the carbohydrates are first rendered soluble. Prolonged action brings about the solution of the cellulose; in this case, dextrose can be detected in the products of hydrolysis. S. B. S.

The Enzymes of Cacao. Harvey C. Brill (*Philippine J. Sci.*, 1915, **10**, 123—133).—The pulp surrounding the cacao bean shows activity for the enzymes casease, protease, oxydase, raffinase, and invertase, whilst the fresh beans gave reactions for casease, raffinase, and very strongly for oxydase. The fermented bean reacts for casease, protease, oxydase, diastase, raffinase, and invertase, and shows the presence of protease and invertase, which are present in the pulp but not in fresh beans.

The conclusion is drawn that the presence of these enzymes influences the character of the fermentation, and that the temperature must be controlled during fermentation so that they may not be destroyed. N. H. J. M.

Chemical Composition of Korean Ginseng. H. Kondo and Tanaka (*J. Pharm. Chim.*, 1915, [vii], **12**, 292—293; from *Yakugakuzasshi*, 1915, *Jul.* 1).—White ginseng yields 47·662% of aqueous extract which contains a substance oxidisable by nitric acid with formation of considerable quantities of mucic acid. The ethereal extract (0·683%) furnishes a volatile oil possessing the odour of ginseng, and a non-volatile portion consisting of a mixture of a phytosterol having $[\alpha]_D + 29·1°$ and m. p. 133°, and an amorphous acid, m. p. 150—156°. The methyl-alcoholic extract of ginseng (25·662%) contains sucrose, a small quantity of a nitrogenous substance, and a glucoside of saponin character which forms a white, hygroscopic powder of pungent taste, melting about 220°. It reduces Fehling's solution only after hydrolysis, when apparently a mixture of dextrose and pentose together with a sapogenin is produced. The latter is likewise a mixture of several substances which have not yet been separated. G. F. M.

Availability of the Nitrogen in Pacific Coast Kelps. Guy R. Stewart (*J. Agric. Research*, 1915, **4**, 21—37).—When mixed with soil, the nitrogen of *Nereocystis luetkeana* is readily converted into ammonia, whilst that of *Pelagophycus porra* is less readily changed. *Macrocystis pyrifera*, the only one of the three which is commercially important in California, changes very slowly in the soil, especially when it has been dried.

Whilst addition of moderate amounts of *Nereocystis* to fresh soil has not much effect on the ammonification or nitrification of readily available organic matter, such as dried blood, the presence of *Macrocystis* retards ammonification, and especially nitrification, for a time, after which they become normal.

In practice it is not probable that kelp or the salts which it contains would interfere with ammonification or nitrification.

N. H. J. M.

Organic Constituents of Pacific Coast Kelps. D. R. HOAGLAND (*J. Agric. Research*, 1915, **4**, 39—58).—Of the total nitrogen of the kelps examined, from one-third to one-fifth is soluble in water, and about the same proportion was found by Stutzer's method to be in the form of non-protein nitrogen. As regards the iodine, only a small proportion seems to be present in organic forms.

The most important of the carbohydrate constituents of kelp is "algin," a very complex resistant compound, or mixture of compounds, of the pentosan type, possibly containing cellulose in the complex.

The total sulphur, which is higher in the leaves than in the stems, varied from 0·45% in the stems of *Nereocystis luetkeana* to 8·16% in *Iridaea*. The relative amount of inorganic and organic sulphur varies considerably in different samples. N. H. J. M.

Carbohydrates and Enzymes of the Soja Bean. J. P. STREET and E. M. BAILEY (*J. Ind. Eng. Chem.*, 1915, **7**, 853—858).—The nitrogen-free extract of soja beans (grown in Ohio) contains the following substances: galactan (including 0·24% from raffinose), 4·86%; pentosan, 4·94%; organic acids (as citric acid), 1·44%; invert-sugar, 0·07%; sucrose, 3·31%; raffinose, 1·13%; starch, 0·50%; cellulose, 3·29%; hemicelluloses, 0·04%; dextrin, 3·14%; waxes, tannins, etc. (by difference), 8·60%. In addition to urease, amylase, and a glucoside-splitting enzyme, soja beans contain a protease of the peptoclastic type, a peroxydase, and a lipase. Sucrase and a peptonising protease do not appear to be present. W. P. S.

Phosphorus Metabolism of Lambs Fed on a Ration of Lucerne, Maize, and Linseed Meal. E. L. ROSS, M. H. KEITH, and H. S. GRINDLEY (*J. Agric. Research*, 1915, **4**, 459—473).—The percentages of the different forms of phosphorus, and the relations of phosphorus to protein, in lucerne, maize, and linseed meal show marked differences. In lucerne, a large proportion of the phosphorus is in inorganic form, soluble in acid; in maize it is equally divided between acid-soluble, which is largely organic, and acid-insoluble; and in linseed meal the phosphorus is largely insoluble in acid, whilst the soluble portion is about equally divided between inorganic and organic forms.

With a ration of the three foods, lambs excrete in the urine only 0·2—0·5% of the total phosphorus. The fæces contain relatively small percentages of acid-insoluble phosphorus and relatively high percentages of soluble, inorganic phosphorus.

Indications were obtained that the amount of phosphorus required for the normal growth and fattening of lambs does not exceed 3 grams per day per 100 lbs. live weight. No evidence was obtained of correlation between the amounts of phosphorus re-

tained in the body on the one hand, and the amounts of phosphorus ingested, the amounts of protein ingested, or the body-weights of the lambs on the other.

Variations in the amount of digestible protein consumed, from 1·56 to 3·19 lbs. per 1000 lbs. of live weight per day, have no significant effect on the forms of phosphorus in the fæces, the total phosphorus in the urine, or the total phosphorus stored in the body, expressed in percentage of the total phosphorus ingested.

N. H. J. M.

Antagonism between Anions as Affecting Barley Yields on a Clay-adobe Soil. CHARLES B. LIPMAN and W. F. GERICKE (*J. Agric. Research*, 1915, **4**, 201—218).—Pot experiments in which two crops of barley were grown, with an interval of three months, in soil to which different amounts of sodium chloride, sulphate, and carbonate, respectively, were added; also experiments on antagonism between sodium chloride and sulphate, sodium chloride and carbonate, sodium carbonate and sulphate, and calcium sulphate and sodium sulphate.

In the control experiment, the yield of the second crop was much greater than that of the first, owing to improvement in the soil from alternate wetting and drying and the thorough drying during the period of rest. Small amounts (0·1%) of sodium chloride and of sodium sulphate acted as stimulants on the first crop and as poisons in the second crop, whilst sodium carbonate was not toxic at all, but showed stimulation in concentrations up to 0·3% of the dry weight of the soil.

Antagonism was shown between sodium chloride and sulphate and between sodium chloride and carbonate in the second crop, but not in the first. In the case of sodium carbonate and sulphate, a slight antagonism was shown in the first crop. Both the first and the second crops showed a marked antagonism between sodium sulphate and calcium sulphate.

The pots received insufficient water to give drainage, and practically the whole of the sodium chloride and sulphate could be recovered at the end of the experiments. In the case of sodium carbonate, the highest amount recovered was 25%. N. H. J. M.

Assimilation of Colloidal Iron by Rice. P. L. GILE and J. O. CARRERO (*J. Agric. Research*, 1914, **3**, 205—210).—Water culture experiments with rice in which colloidal iron and ferric chloride were compared as sources of iron. In order to prevent precipitation of the colloidal iron, the nutrient solution was put into one flask and the iron into a second flask, the plants being grown with part of their roots in each flask. The colloidal iron employed was the ordinary dialysed iron, and contained some chlorine.

The plants supplied with colloidal iron assimilated a small amount of iron, probably soluble iron, which must be assumed to be present. The conclusion is drawn that colloidal iron was not assimilated, and that if roots secrete acids at all there was at any rate no secretion in the unbalanced solution employed. In the

flasks containing iron alone the root development was very poor, but better with colloidal iron than with ferric chloride, which produced less growth than distilled water. The toxicity of distilled water and of ferric chloride cannot be overcome by supplying other roots of the same plant with a balanced solution.

The question is of importance, because upland rice grown on more or less calcareous soils is affected with chlorosis, due, at least in part, to diminished assimilation of iron. N. H. J. M.

The Character of the Water-soluble Nitrogen of Some Common Feeding Stuffs. E. B. HART and W. H. BENTLEY (*J. Biol. Chem.*, 1915, **22**, 477—483).—The "amide" nitrogen of feeding-stuffs is largely composed of free amino-acids and peptide linkings. In most cases this nitrogen constitutes 50—70% of the water-soluble nitrogen. The acid amide nitrogen is relatively small, usually under 10%; corn stover is an exception, the figure there being 40%. The ammonia nitrogen rarely exceeds 5%, and is sometimes absent. The substances investigated include clover, peas, corn, barley, rape, grasses, and cabbage. W. D. H.

Soil Gases. J. WALTER LEATHER (*J. Agric. Sci.*, 1915, **7**, 240—241).—From the results of experiments with undisturbed and ordinary samples of Pusa soil, which were subjected to the treatment described by Russell and Appleyard (*ibid.*, 5), the conclusion is drawn that the gas obtained on successive days by Russell and Appleyard was formed and liberated gradually, presumably by bacterial action. N. H. J. M.

[Soil Gases.] A. APPLEYARD and E. J. RUSSELL (*J. Agric. Sci.*, 1915, **7**, 242).—In reply to Leather (preceding abstract), it is pointed out that the successive extractions were not made on successive days, and that in some cases there were practically no intervals between them.

The conclusion previously drawn, that the dissolved gas in the surface films of water consists mainly of carbon dioxide and a little nitrogen, is supported by the results obtained with the Pusa soil, which also yielded small amounts of gas poor in oxygen. N. H. J. M.

Changes in the Soil brought about by Heating. (MISS) A. WILSON (*Sci. Proc. Roy. Dubl. Soc.*, 1915, [N. S.], **14**, 513—520).—Soils which were heated at temperatures from 60° to 150° showed a regular depression in the freezing points of its aqueous extracts, which increased from 0·06° in the case of soil heated at 60° to 0·19° in the soil heated at 150°; coincidently, the electrical conductivities of the extracts showed an increase from $36·0 \times 10^{-5}$ to 198×10^{-5}. It is therefore evident that the amount of soluble matter is increased by heating.

Whilst extracts of the original soil were practically colourless, the extracts of the heated soil varied from a faint brownish-yellow colour (60°) to a very deep brown (150°). Soils which were heated

at the higher temperatures absorbed more water than unheated soils.

Experiments in which the soil extracts were prepared by stirring the soils with water and filtering, instead of by percolation, gave similar results.

The conclusion is drawn that the increased fertility of heated soils may be partly due to the increase in soluble constituents and to the change in soil texture resulting in an increased power of retaining water. N. H. J. M.

Effect of Alkali Salts in Soils on the Germination and Growth of Crops. Frank S. Harris (*J. Agric. Research*, 1915, **5**, 1—53).—The effect of alkali salts varies with different soils and different plants. In sand, only about half as much alkali is required to inhibit growth as in loam, whilst the power of plants to resist the action of alkali salts diminishes in the following order: barley, oats, wheat, lucerne, beet, maize, and Canada field peas.

The toxicity of alkali salts in soils is determined by the acid radicle, chlorides being the most toxic. Of the bases, sodium is the most toxic. The toxicity of soluble salts in the soil was found to be in the following order: sodium chloride, calcium chloride, potassium chloride, sodium nitrate, magnesium chloride, potassium nitrate, magnesium nitrate, sodium carbonate, potassium carbonate, sodium sulphate, potassium sulphate, and magnesium sulphate.

The following approximate amounts of soluble salts will probably indicate the necessity of reclamation to produce ordinary crops. In loam, chlorides 0·3, nitrates 0·4, carbonates 0·5, and sulphates more than 1%. In coarse sand the amounts should not exceed about two-thirds of the numbers given for loam.

The antagonistic effects of combined salts is less in soil than in water-cultures. N. H. J. M.

Amino-acid Nitrogen of Soil and the Chemical Groups of Amino-acids in the Hydrolysed Soil and their Humic Acids. R. S. Potter and R. S. Snyder (*J. Amer. Chem. Soc.*, 1915, **37**, 2219—2227).—An account is given of the examination of several samples of soil. In each case the soil was first extracted with 1% hydrochloric acid to render the humus more soluble, and the amount of nitrogen extracted by the acid estimated. The soil was hydrolysed with 22% hydrochloric acid, and the mixture was filtered, and the residue washed until free from chlorides. A portion of the combined filtrate and washings was employed for the estimation of total nitrogen, whilst other portions were examined by van Slyke's method (A., 1910, ii, 751) for the determination of the chemical groups of amino-acids. The humic acids were removed from the acid-extracted soil by means of 1% sodium hydroxide; the alkaline solution was neutralised with sulphuric acid, and then acidified with acetic acid. The mixture was boiled for fifteen minutes, and the precipitated humic acids were collected and hydrolysed with 22% hydrochloric acid. The product of

hydrolysis was examined by van Slyke's method, and the total nitrogen was also estimated.

The results show that the amounts of nitrogen extracted by the strong acid were fairly constant, whilst those extracted by the dilute alkali varied widely. The quantities of humic acid in the various soils were quite different. The amount of amide nitrogen in the soils was in all cases very high in comparison with the basic and non-basic nitrogen. The quantity of humic nitrogen extracted from the soil by dilute alkali was very large when compared with the amounts in proteins. The relative proportions of the various groups in the extract obtained with the strong acid and in the humic acids were very similar, and it is evident that dilute alkali does not extract any typical class of organic compounds from the soil. It is considered that the estimation of the amount of humus is of little value in soil analysis. The quantity of amino-acid and peptide nitrogen existing in a soil is very small in comparison with the amounts of amino-acids produced by hydrolysis. E. G.

A Nitrogenous Soil Constituent: Tetracarbonimide. EDWARD C. SHOREY and E. H. WALTERS (*J. Agric. Research*, 1914, **3**, 175—178).—In 1913 a compound having the properties of tetracarbonimide was isolated from several soils (*J. Wash. Acad. Sci.*, 1913, [v], **3**, 260). The substance has now been obtained in a pure state, and compared with tetracarbonimide from uric acid.

Tetracarbonimide was found in soils from Florida, Virginia, Maryland, and Washington, D.C. From 18 kilos. of the latter soil 30 mg. of the pure compound were obtained, and as the loss in purification is at least 50%, it is estimated that the upper 12 inches of the soil contains about 8 kilos. of tetracarbonimide per hectare.

As uric acid has not been found in soils or plants, it seems probable that the tetracarbonimide in soils is derived from purine bases. Xanthine, hypoxanthine, and adenine all occur in soils, whilst guanine has been found in a heated soil. All four bases have been found in plants. N. H. J. M.

Presence of Proteoses and Peptones in Soils. E. H. WALTERS (*J. Ind. Eng. Chem.*, 1915, **7**, 860—863).—It is shown that soils contain a mixture of proteoses and peptones resulting from the hydrolysis of proteins, and that they either exist and persist in the soil as such for a considerable period, or the original protein is hydrolysed only very slowly in the soil. W. P. S.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

Some Deductions from Lord Rayleigh's Formula for Turbid Media. A. BOUTARIC (*J. Chim. phys.*, 1914, **12**, 517—525).—According to the formula in question, the effect of the addition of small particles to a homogeneous medium is to alter the refractive index from μ_0 to μ, such that $\mu-\mu_0=nT(D'-D)/2D$, where n is the number of particles per c.c., T the volume of each particle, D the optical density of the homogeneous medium, and D' that of the particles. The author applies this formula to gases on the assumption that these may be regarded as suspensoid systems, and shows that this leads to the relation $T=2(\mu-1)/3n$. According to this, the volume of the molecules of different gases is proportional to the excess of the refractive index over unity. It follows, further, that the density of the gas molecules is given by $d'=673\cdot10^{-7}M/(\mu-1)$, where M is the molecular weight of the gas. The values obtained from this equation are of the same order of magnitude as the densities of solid substances, and range from 2·1 for cyanogen to 20 for neon.

The formula is also applied to liquid solutions, and the density of the molecules of the dissolved substance is shown in this case to be given by $d'=3C/2000(\mu-\mu_0)$, in which C is the concentration of the dissolved substance in grams per litre. The density numbers obtained from this equation are recorded for a number of salts. The lowest value, 4·7, was found for ammonium nitrate, and the highest, 13, for thallous sulphate. H. M. D.

High-Frequency Spectra of the Elements. IVAR MALMER (*Phil. Mag*, 1914, [vi], **28**, 787—794. Compare Moseley, A., 1914, ii, 14, 326).—The high-frequency spectrum measurements of Moseley have been extended by the author so as to include the frequencies of the characteristic radiation of the K series which is emitted by yttrium, zirconium, molybdenum, ruthenium, palladium, silver, cadmium, iridium, tin, antimony, barium, lanthanum, and cerium. These elements form a series in which the atomic number N increases from 39 (yttrium) to 58 (cerium).

In agreement with Moseley's observations, it is found that when the square root of the frequency is plotted as a function of the atomic number, a straight line is obtained. In general, the agreement with the linear relation is within the limits of experimental error, but for antimony this is not the case. The anomaly disappears if the atomic number of antimony is taken as 52 instead of 51. Since for antimony $N=51$, when radiation of the L series is emitted, it would seem that the atomic number of an element may vary according to the type of radiation which it emits.

For the elements from aluminium to zinc, Moseley found that the relation between the frequency ν of the α-line and the atomic number can be expressed by $\nu=\frac{3}{4}\nu_0(N-1)^2$, in which ν_0 is Rydberg's constant. The author's observations show that this formula does not hold good throughout the series of the elements.

H. M. D.

Flame Reactions. III. WILDER D. BANCROFT and HARRY B. WEISER (*J. Physical Chem.*, 1914, **18**, 762—781. Compare A., 1914, ii, 317).—The authors show that a luminescence is produced at the anode during the electrolysis of certain salts with a number of different metals as anodes. These reactions have been studied in the case of solutions of potassium chloride, iodide, bromide, and sulphate, using anodes of mercury, tin, cadmium, silver, and lead. In most cases a decided luminescence was obtained, and in every case where such electroluminescence appeared, a firm, coherent film was previously formed on the anode. In certain cases in which the product of the anodic reaction was soluble in the electrolyte, the film formation was delayed for some time, and in these cases no luminescence appeared until after the film was formed. The luminescence was not due either to the thermoluminescence of the film or to a sparking through the film; it was situated under the film in the anode reaction zone. A poorly conducting film is necessary, since the heat generated by its resistance to the current causes a local rise of temperature at the surface of the anode; this heats, and presumably volatilises, a portion of the metal of the anode, which reacts with the nascent anion and produces the luminescence. No luminescence was obtained unless the metal anode, in corroding, formed a solid salt instead of dissolving or disintegrating. Ordinarily, the solubility is least, and the stability greatest, in cold solutions, and consequently it is to be expected that the luminescence would be greater in cold solutions than in hot solutions. This is particularly noticeable in the electrolysis

of potassium bromide with a mercury anode. In many instances the heated metal will burn brightly in an atmosphere of oxygen or one of the halogens, and the light emitted under these conditions is of the same colour as the light emitted by the same substances when they react in an electrolytic cell. With a stationary anode, the luminescence is usually only a flash, since the film masks the luminescence and diminishes the current, so that the velocity of reaction is very low. In most cases the luminescence can be made continuous by rotating the anode rapidly, and at the same time brushing it with a stiff brush, so that the film does not become too thick. J. F. S.

Optical Rotatory Power and Chemical Constitution. L. G. WESSON (*J. Amer. Chem. Soc.*, 1914, **36**, 2522—2532).—Pickard and Kenyon have studied the rotatory power of members of several homologous series of optically active compounds, and have explained their results by means of a hypothesis based on a consideration of the space occupied by the four groups attached to the asymmetric carbon atom (T., 1913, **103**, 1930).

In the present paper it is suggested that the phenomena of optical activity depend primarily on the attractive forces exerted on an asymmetric atom by its four adjacent atoms or groups rather than on the space occupied by these atoms or groups. This view is deduced from the experimental data published by Pickard and Kenyon. E. G.

Kinetics of Photochemical Reactions and the Law of Radiation. A. SCHIDLOF (*Arch. Sci. phys. nat.*, 1914, [iv], **38**, 97—112. Compare A., 1914, ii, 601).—A theoretical paper in which the quantum theory is applied in the deduction of the laws of radiation and photochemical equilibrium. The velocity of a photochemical reaction is supposed to depend on the mean energy of the molecules which act as resonators, and also on the characteristic vibration frequency. H. M. D.

Method of Treating Radioactive Barium Compounds. H. N. MCCOY (U.S. Pat. 1103600; from *J. Soc. Chem. Ind.*, 1914, **33**, 919).—The separation and concentration of radioactive substances, such as radium, mesothorium-*I* and thorium-*X*, from barium compounds is effected by converting the barium and the radioactive elements into hydroxides, and fractionally separating barium hydroxide from the solution. The partial precipitation of the hydroxides of barium and of the radioactive elements is accomplished preferably by adding alkali hydroxide. C. S.

The Distribution of the Active Deposit of Actinium in an Electric Field. A. N. LUCIAN (*Phil. Mag.*, 1914, [vi], **28**, 761—778; *Amer. J. Sci.*, 1914, [iv], **38**, 539—555).—The recent results of Walmsley (A., 1913, ii, 905) on the distribution of the active deposit of actinium in an electric field being at some points in contradiction to those of Wellisch (*ibid.*) for the active deposit of

radium, the question has been re-examined, and the following conclusions reached: (1) In dust-free, dry air the percentage of actinium active deposit collected on the cathode increases with increasing potentials to a definite limit of 95% as the maximum, the remaining 5% consisting of neutral particles, which arrive at the electrodes by diffusion. (2) No negative particles take part in the distribution. (3) For lower values of the cathode deposit, the formation of neutral deposit particles results both by volume recombination and columnar recombination of the positively charged particles with negative ions. Both types of recombination occur at a faster rate for the deposit particles than for ordinary positive ions, due to their larger mass and size and slower speed. In all respects the actinium active deposit behaves, qualitatively at least, like that of radium. It is supposed that the recoiling deposit particle, in its collision with the molecules in its path, expels from them negative electrons with much greater velocity than is imparted to the positive ion, so that the recoil particle is surrounded by an overwhelming majority of positive ions, and there is a greater probability that it will emerge positively charged than otherwise. The fact that the limiting value for the cathode deposit is for actinium (95%) greater than for radium (88%) is what is to be expected from the fact that the actinium-*A* atom recoils with a greater velocity than the radium-*A* atom. Since the recoil velocity of the thorium-*A* atom is intermediate, it is to be expected that the limiting value for the thorium cathode deposit will lie between 88 and 94%. F. S.

The Transformations of Actinium-*C*. R. W. VARDER and E. MARSDEN (*Phil. Mag.*, 1914, [vi], **28**, 818—821).—Confirmation of the existence of a small proportion of α-rays from actinium-*C*, more penetrating than the rest, has been obtained by an ionisation method. A pencil of α-particles from a source of actinium active deposit fell on the usual Bragg ionisation apparatus. At a range beyond 5·4 cm., the range of the ordinary α-rays of actinium-*C*, a small ionisation was observed. A powerful magnetic field was used to deviate β-rays. Comparative experiments with radium-*C*, thorium-*C*, and actinium-*C* showed a clear difference in the latter case, confirming the existence of a branch product of actinium-*C* involving the emission of α-rays of 6·45 cm. range by 0·2% of the atoms disintegrating. That these α-particles were not due to impurity was shown by the ionisation they produce, decaying with the period of thirty-six minutes, in agreement with that of the actinium active deposit as a whole. F. S.

Process for Obtaining Radiothorium or Substances Containing it for the Preparation of Solutions Containing Thorium-*X*. DEUTSCHE GASGLÜHLICHT AKTIEN-GESELLSCHAFT (D.R.-P. 269692; from *J. Soc. Chem. Ind.*, 1914, **33**, 312).—The solution of the material, freed as far as possible from impurities, especially barium, calcium, iron, lead, phosphoric acid, and, if practicable, cerite earths, is treated with pure ammonia and the

precipitate washed and dissolved in dilute nitric acid; the liquid is then evaporated to dryness to expel the excess of acid, and the aqueous solution of the residue treated with excess of pure ammonia. The precipitated hydroxides, containing radiothorium, are evaporated to dryness, together with the solution of ammonium salts, the latter being removed from the dry residue by repeated washing with either water or a dilute sodium chloride solution free from carbon dioxide. Solutions containing thorium-*X* are prepared by leaving the residue, obtained as described above, in contact with pure, distilled water or with dilute sodium chloride solution free from carbon dioxide until a sufficient quantity of thorium-*X* has passed into solution. T. H. P.

Lead and the End Product of Thorium. I. ARTHUR HOLMES and ROBERT W. LAWSON (*Phil. Mag.*, 1914, [vi], **28**. 823—840).—To test the question whether thorium-*E*, the end-product of thorium, is a stable isotope of lead, the thorium content of some Devonian minerals, for which the uranium and lead content were known from previous work, has been examined. If thorium-*E* is a stable isotope of lead, the ratio Pb/(U + 0·4 Th) should be constant, where Pb is the amount of lead, U and Th the average amounts of uranium and thorium in the mineral, during the time the mineral has been in existence, the rate of production of lead from thorium being 0·4 times that of lead from uranium. The thorium was estimated radioactively by Mache's method (*Sitzungsber. K. Akad. Wiss.*, 1914, **123**, 334), by comparing the emanation liberated from the solutions, obtained by fusing the mineral with sodium carbonate, with that from solutions of standard thorium minerals, in which the thorium has been determined by analysis.

The minerals were all from the Langesund Fjord district, south of Christiania, and of Devonian age, being almost certainly Middle Devonian. The ratio of thorium to uranium varied between very wide limits over a range of 120 times. But, with two exceptions, the lead–uranium ratios were remarkably constant at 0·04, as a representative value, and independent of the thorium content. There was no indication of constancy in the lead–thorium ratios, and the conclusions are drawn that radium-*G* is a stable isotope of lead, that radium-*G* and thorium-*E* cannot both be stable, and therefore that thorium-*E* is unstable.

Existing analyses of various minerals are examined, and it is shown that the lead–uranium ratio is independent of the proportion of thorium present. The various recent atomic weight determinations of lead from radioactive minerals are discussed.

F. S.

The Volatility of Thorium-*D*. Relative β-Activities of Thorium-*C* and -*D*. A. B. WOOD (*Phil. Mag.*, 1914, [vi], **28**, 808—818).—Pure thorium-*D* obtained by recoil, after measurement of its amount by a β-ray electroscope, was heated in an electric furnace for four minutes at a definite temperature, and again measured. After allowance for the exponential decay, the propor-

tion volatilised could be evaluated. For untreated thorium-*D*, volatilisation commenced at about 520°, and the proportion volatilised increased linearly with rise of temperature to 700°, when the whole was volatilised. Treating the recoiled thorium-*D* with nitric acid and evaporating to dryness produced no change in the volatility, showing that the thorium-*D* after this treatment is left in the same form as when deposited by recoil. But after heating with hydrochloric acid, volatilisation commenced at 270°, and was complete below 500°, the curve running parallel with that for the untreated thorium-*D*. This is in accord with Schrader's observation that the chlorides of the active deposit radio-elements are more volatile than the untreated deposits.

Thorium-*D*, recoiling from thorium active deposit which has been treated with hydrochloric acid, volatilises as untreated thorium-*D*, and the same result is obtained for thorium-*D* recoiling from pure thorium-*C* which has been dissolved in hydrochloric acid and evaporated to dryness. This shows that thorium-*D* recoils in atomic form, and not as chloride.

The volatilisation of thorium-*D* from the active deposit from evaporated nitric acid solution is the same as from untreated active deposit. Volatilisation commenced at 500°. But from the active deposit dissolved in hydrochloric acid and evaporated, volatilisation commenced at temperatures between 300° and 500°, even from active deposit in which all the thorium-*D* chloride initially present had had time to decay. It would appear that in this case a combination of the thorium-*D* with chlorine occurs after its production.

Thorium-*C* volatilises at 780°, and at 700° a complete separation of thorium-*C* and -*D* may be effected by volatilisation. The ionisation produced by thorium-*C* is about 1·5 times that produced by thorium-*D*. F. S.

Mechanism of the Chemical Action of Electric Discharges. I. General Considerations. E. Briner (*J. Chim. phys.*, 1914, **12**, 526–533).—The author considers that the chemical effects produced by the passage of the electric discharge through gases are due to the action of three agencies, namely, high temperature, the liberation of electrons, and the emission of ultra-violet rays, when the hard β-rays are compared. H. M. D.

Mechanism of the Chemical Action of Electric Discharges. II. Formation of Ammonia. E. Briner and J. Kahn (*J. Chim. phys.*, 1914, **12**, 534—563. Compare preceding abstract).—In order to ascertain the nature of the action involved in the chemical changes which occur on the passage of electricity through certain gases, the authors have investigated the influence of various types of discharge on the formation of ammonia. In these experiments, mixtures of nitrogen and hydrogen in the ratio $N_2 : 3H_2$ were subjected to the influence of spark, arc, and silent discharge, and on the attainment of the stationary condition, the proportion of ammonia formed was estimated from the observed change in volume or pressure.

At constant temperature and varying pressure, the proportion

of combined nitrogen attains a maximum at about 100 mm. in the case of both spark and arc discharge. When the silent discharge is used, the proportion of combined nitrogen is much smaller. On this account, the accuracy attained is not so great, although it is quite sufficient to show that the connexion between the proportion of combined nitrogen and the pressure differs considerably from that found in the spark and arc discharge. As the pressure falls from 700 to about 150 mm., the proportion of combined nitrogen decreases, and then increases rapidly when the pressure is further reduced to 100 mm.

Observations with the arc discharge show that the proportion of combined nitrogen increases with the strength of the current, but the effect produced by successive equal increments of the current becomes gradually smaller. From experiments at temperatures between $-35°$ and 500°, it appears that the proportion of combined nitrogen has a minimum value at about 100° and a maximum at about 300°. At a pressure of 700 mm., the closer approach of the electrodes leads to a diminution in the proportion of combined nitrogen, but at 100 mm. the distance between the electrodes has very little influence on the condition of "equilibrium." When the volume of the apparatus is increased, the proportion of combined nitrogen undergoes a diminution.

The authors anticipate that these observations may help to throw some light on the mechanism of the chemical change.

H. M. D.

The Electrolytic Dissociation of Acetylene and its Metallic Derivatives. M. Skossarewsky (*Compt. rend.*, 1914, **159**, 769—771).—The author has studied the variations of the molecular conductivity of acetylene with the concentration of the solution, the thermal coefficient of conductivity, and the electrolysis of monosodium acetylide, using liquid ammonia as a solvent. Measurements were made for the first two points at $-45°$ and 0°. The results show that the dissociation of acetylene increases with the dilution of the solution, and that the thermal coefficient of conductivity is about 2% for each degree, and almost independent of the concentration of the solution.

The molecular conductivity of sodium acetylide, C_2HNa, at medium concentrations is of the same order as that of sodium acetate in aqueous solution. Electrolysis takes place, sodium being liberated at the cathode, and a mixture of products at the anode, one fraction of which is gaseous at $-50°$. After a few minutes' electrolysis, the electrodes are strongly polarised, the *E.M.F.* of polarisation being 2·71 volts. If the electrolysis is continued, the sodium in solution in the ammonia diffuses to the anode, and forms a short circuit in the electrolytic cell. Examination of the gaseous products showed the presence of acetylenic and ethylenic hydrocarbons.

W. G.

Electromotive Forces and Electrode Potentials in Mixed Solvents. J. N. Pearce and W. H. Farr (*J. Physical Chem.*, 1914, **18**, 729—758).—The electrode potentials of silver in solutions of

silver nitrate in water, ethyl alcohol, methyl alcohol, and in a series of binary mixtures of these solvents, have been determined at 0° and at 25°. The electrode potentials are greatest in methyl alcohol and least in aqueous solution. The values of the electrode potentials are highest in the most concentrated solutions, and on dilution they decrease rapidly at first, and then on further dilution they decrease further in an almost linear manner. The electrode potentials in the binary mixtures of the two alcohols obey the law of mixtures. In the binary mixtures of water and the two alcohols, the electrode potentials increase slowly at first with addition of the alcohol from the value in pure water up to mixtures containing about 75% of the alcohol, and then more rapidly with further increase in the proportion of alcohol. The temperature-coefficients have been calculated for each concentration in each solvent used. In both of the alcohols and their binary mixtures, the temperature-coefficients are positive. Those in ethyl alcohol, 75% ethyl alcohol–methyl alcohol, and 50% ethyl and methyl alcohols increase with dilution, whilst the temperature-coefficients in methyl alcohol and its 75% mixture pass through a minimum value. The temperature-coefficients in the water and 75% aqueous solutions are negative, and the values of these negative coefficients increase with dilution. The influence of the water, as manifested by the temperature-coefficients, is displaced toward higher dilutions as the proportion of the alcohol in the mixture is increased. The *E.M.F.* of all the possible concentration cells in all the above solvents have been determined and compared with those calculated from the electrical conductivities by means of the Nernst equation. From the agreement between the observed and the calculated *E.M.F.*, it can be seen that the Nernst equation can be applied, not only to solutions in non-aqueous solvents, but also to solutions in binary mixtures of these solvents. The solution tension of silver in each of the three solvents has been calculated, and found to be: in water, $3{\cdot}91 \times 10^{-17}$; in ethyl alcohol, $5{\cdot}94 \times 10^{-18}$; and in methyl alcohol, $1{\cdot}98 \times 10^{-19}$. The heats of ionisation were calculated for the pure solvents and for the 50% mixtures, and found to be: in ethyl alcohol, +22,727 cal.; in methyl alcohol, +23,126 cal.; in water, 24,063 cal.; in 50% ethyl alcohol–water, +24,293 cal.; in 50% methyl alcohol–water, +24,541 cal.; and in 50% ethyl alcohol–methyl alcohol, +22,973 cal. J. F. S.

Magnetochemistry of the Salts of Copper, and the Magneton Theory. I. Cupric Chloride, Nitrate, and Sulphate in Concentrated Solution. B. Cabrera and E. Moles (*Anal Fis. Quim.*, 1914, **12**, 373—379).—Determinations of the magnetic susceptibility of cupric chloride, nitrate, and sulphate have yielded values in fair agreement with the law of Liebknecht and Wills (A., 1900, ii, 187). A. J. W.

Magnetic Investigation of the Changes of Structure of Iron and Chromium Compounds at High Temperatures. Kôtarô Honda and Také Soné (*Sci. Rep. Tohoku Imp. Univ.*, 1914, **3**, 223—234. Compare A., 1914, ii, 526).—The influence of tempera-

ture on the magnetic susceptibility of hæmatite, magnetite, chromium trioxide, and chromium sesquioxide has been examined over the range $-170°$ to $1300°$. From the susceptibility-temperature curves of the iron compounds, the authors draw the conclusion that hæmatite shows no change of structure up to $1300°$, and that it contains a small quantity of magnetite at temperatures above $-40°$. If magnetite is heated in air at $1300°$, it is almost completely converted into hæmatite. Chromium trioxide appears to undergo two changes, whereby the oxide, Cr_6O_{15}, is formed at about $290°$, and Cr_2O_3 at about $420°$. The curve for chromium sesquioxide indicates that no change of structure occurs up to $1300°$.

H. M. D.

Deduction of Maxwell's Generalised Law by the Statistical Method. A. Berthoud (*J. Chim. phys.*, 1914, **12**, 564—579. Compare A., 1911, ii, 578).—It is shown that the law of distribution of the molecules of a gas in respect of temperature may be derived from the Boltzmann-Gibbs formula by application of the statistical method. In this deduction, it is assumed that the specific heat of the gas is constant. H. M. D.

Specific Heat of Copper in the Interval 0° to 50°. Vacuum-Jacketed Calorimeters. D. R. Harper (*J. Washington Acad. Sci.*, 1914, **4**, 489—490).—The specific heat of copper has been determined by suspending a coil of copper wire in a vacuum, and heating it by an accurately measured current for a measured time. To arrange a sufficient amount of the copper in a form suitable for electrical measurement, the wire is coiled into spirals about 150 cm. in length; thirty-two of these, superposed with mica plates between, built up a cylinder, 10 cm. by 10 cm., containing about 2 kilo. of copper and having a resistance of about 0·2 ohm. The increase in the temperature of the wire is determined by using it as a resistance thermometer. The result of twenty-seven determinations is given as $0·3834 + 0·00020(t - 25)$ international joules per gram degree, which is equivalent to $0·0917 + 0·000048(t - 25)$ calories per gram degree between the temperatures 15° and 50°. The efficacy of the vacuum jacket in reducing the magnitude of the cooling correction was not so good as was anticipated. J. F. S.

Specific Heats of Liquids and Vapours at Constant Pressure and Volume. Stefano Pagliani (*Nuovo Cim.*, 1914, [vi]; **8**, ii, 157—188).—The author compares his earlier results (1883—1890), recalculated on the basis of experimental data concerning specific heats published since 1884, with those obtained by Tyrer (T., 1913, **103**, 1675; A., 1914, ii, 425).

Within the limits of temperature employed, the specific heats at constant volume for most of the sixteen liquids for which data are available increase with rise of temperature, but water, carbon tetrachloride above 30°, and carbon disulphide above 10° are exceptions to this rule; Tyrer's statement, that the extent of this increase rises with the number of atoms in the molecule of the liquid, is not verified. For water, just as for the liquids examined by

Tyrer, the specific heat at constant volume for the liquid is greater than that for the vapour at the same temperature. Although the specific heat of water, unlike those of the other liquids, decreases with rise of temperature, that for water vapour exhibits a diminution similar to those for the other vapours, the differences being generally very small.

As a rule, the difference between the two specific heats, which is equivalent to the work of thermal expansion, is greater for a liquid than for its vapour at the same temperature, yet for water and for methyl alcohol the value of this difference for the liquid coincides with that for the vapour at a certain temperature; at lower (or higher) temperatures, the difference is less (or greater) for the liquid than for the vapour. These results seem to corroborate the view that the energy absorbed during the expansion of a liquid is mainly employed, not in overcoming the external pressure, but in effecting internal work necessitated by the intermolecular attraction or in increasing the molecular energy.

Tyrer's general relation, that the difference between the two specific heats increases continuously with rise of temperature, does not hold for certain liquids; thus, for carbon tetrachloride, it is valid only above 20°, and for chlorobenzene only above 50°, whilst with toluene, xylene, and cymene this difference varies in the opposite sense. Conclusions in support of, or against, the de Heen hypothesis cannot, therefore, be drawn from these variations. Further, for all normal liquids, the value of the expression $(c_p - c_v)v^2/(dv/dt)$ is not constant, but variable, so that here again Tyrer's conclusions are invalid.

Also, the product of the molecular weight and the factor $(c_p - c_v)$ is not constant for normal liquids at one and the same temperature, although the values of this product for members of any one chemical series are of similar orders of magnitude. The expression $l.(dv/dt)/v(c_p - c_v) = 1$ (compare Tyrer, *loc. cit.*) is not of general application.

Neither the relation deduced by Tyrer, who found that the ratio between the two specific heats remains constant for all liquids, nor that of Lussana (A., 1914, ii, 764), who stated that this ratio always diminishes with rise of temperature, is confirmed; increases of the ratio are, indeed, observed for water between 0° and 100°, for ethyl alcohol above 20°, for amyl alcohol above 40°, for chloroform above 20°, for carbon tetrachloride above 30°, and for carbon disulphide between 0° and 40°.

In general, although not invariably, this ratio decreases with increase in the molecular weight in a homologous series. Increase with the density is not universally the case, since, within certain ranges of temperature, increase of the ratio with rise of temperature occurs with such liquids as water, benzene, ethyl or *iso*amyl alcohol, chloroform, carbon tetrachloride, or carbon disulphide. Tyrer's results furnish no demonstration of the Dupré-Amagat equation; his expression, $\beta = T(dv/dt)v/C_1$, exhibits mere analogy of form to this equation, and is not verified by experiment.

T. H. P.

Coefficients of Fluidity Temperatures, and their Relation to Heat of Fusion. J. GUZMÁN CARRANCIO (*Anal. Fis. Quim.*, 1914, **12**, 432—447).—A theoretical paper on heat of fusion, in which the author summarises and discusses results previously published. A. J. W.

Vapour Pressure of Solutions. Static Method for the Determination of the Difference Between the Vapour Pressure of Solution and that of Solvent. J. C. W. FRAZER and B. F. LOVELACE (*J. Amer. Chem. Soc.*, 1914, **36**, 2439—2449).—The importance of the accurate determination of the effect of dissolved substances on the vapour pressure of solvents, and the lack of agreement in the results of different workers using dynamic methods, have led the authors to improve the static method.

The apparatus employed consists essentially of a Rayleigh manometer (A., 1901, ii, 542), one side of which is in communication with the bulb containing the solvent, and the other with the bulb containing the solution. Experiments made with solutions of mannitol have shown that, in order to ensure accuracy, the variations of temperature of the solution and solvent must not exceed 0·002°, but that accurate regulation of the temperature of other parts of the apparatus, namely, those parts containing vapour, is not necessary. If the temperature of the bath in which the bulbs are immersed is controlled to within 0·001°, the pressure readings are constant to within 0·001 mm. E. G.

Vapour Pressures of Certain Alcoholic Solutions. O. F. TOWER and A. F. O. GERMANN (*J. Amer. Chem. Soc.*, 1914, **36**, 2449—2456).—A method for measuring vapour pressures by means of the Morley mercury gauge has been described by Tower (A., 1908, ii, 811). The present paper gives an account of certain improvements in the apparatus and in the method of treating the solutions for the determination of the vapour pressures of non-aqueous solutions.

Measurements have been made in which methyl and ethyl alcohols were used as solvents, and potassium iodide, lithium chloride, and benzil as solutes, and the molecular weights of the solutes have been calculated from the results. In the case of potassium iodide and lithium iodide, the molecular weights are less than the formula weights, and the values show a remarkable constancy throughout the different dilutions. In other words, the calculated molecular weights do not indicate that the salts are more dissociated in dilute solutions than in concentrated, and this is confirmed by Jones' ebullioscopic measurements with potassium iodide in methyl and ethyl alcohols (A., 1900, ii, 187). The molecular weight of benzil in ethyl alcohol seems to be constant, whilst in methyl alcohol the compound appears to be associated with one or two molecules of the solvent. E. G.

Partial Vapour Pressures of Ternary Mixtures of Toluene, Carbon Tetrachloride, and Ethylene Dibromide. M. A. ROSANOFF, JOHN F. W. SCHULZE, and R. A. DUNPHY (*J. Amer. Chem. Soc.*, 1914, **36**, 2480—2495).—This work was undertaken in

connexion with a study of fractional distillation with regulated still-heads. The effect of the regulated still-head on vapours containing more than two components has not yet been investigated, and in order to render such an investigation possible it was necessary (1) to devise a method for the rapid and accurate analysis of consecutive fractions of a ternary distillate, and (2) with a view to discover the law involved, to determine the partial pressures of the ternary mixtures of a suitable set of three substances at the boiling points of the mixtures under ordinary atmospheric pressure. A suitable analytical method has already been described by Schulze (A., 1914, ii, 300), and measurements have now been made of the partial vapour pressures of various mixtures of toluene, carbon tetrachloride, and ethylene dibromide. For the purpose stated, it was necessary to determine the vapours in equilibrium with the various ternary liquids boiling at least at some one temperature, and this has been done for the five temperatures 83°, 91°, 99°, 107°, and 115°. For each of these temperatures, five different ternary mixtures and the two binary mixtures, all boiling at that temperature, were studied. The results are tabulated, and also represented graphically. E. G.

Free Energy of the Various Forms of Elementary Sulphur. GILBERT N. LEWIS and MERLE RANDALL (*J. Amer. Chem. Soc.*, 1914, **36**, 2468—2475).—Calculations of the free energy of sulphur have been made from existing data, and have given the following values (in calories) of the free energy of formation ($\Delta F°298$). Solid sulphur, rhombic form, 0; monoclinic form, 17·5. Liquid sulphur, $S\lambda$ 94; the equilibrium mixture $S\lambda,\mu$, −0·8. Gaseous sulphur, S_2, 17,600. E. G.

Thermostat for Low Temperatures. JAMES H. WALTON, jun. and ROY C. JULD (*J. Physical Chem.*, 1914, **18**, 717—721).—A thermostat is described for temperatures between 0° and −20°. It consists of two galvanised iron vessels which are placed in larger wooden boxes, and the spaces between are filled, respectively, with sawdust and felt. The two vessels are connected by a pipe, through which a strong brine solution is pumped from the larger vessel to the thermostat proper. The connecting pipe is fitted with an electrically regulated stopcock, which is operated by a temperature regulator in the thermostat. For temperatures between 0° and −20°, the thermostat is filled with a mixture of two parts of water, one of glycerol, and one of ethyl alcohol. The temperature regulator consists of a steel tube filled with mercury, which is fitted with a special device for overcoming lag of temperature. By using a mixture of ice and calcium chloride instead of brine, the temperature can be kept constant at −30°. The temperature by means of this instrument can be kept within ±0·03°. J. F. S.

Modified Precision Barometer. ALBERT F. O. GERMANN (*J. Amer. Chem Soc.*, 1914, **36**, 2456—2462).—A form of precision barometer is described in which both pump and barometer are

combined into one instrument. It consists of a modification of the mercury pump described by Germann and Cardoso (A., 1912, ii, 933), in which the main reservoir has been omitted, and is particularly serviceable for determination of the densities of gases.

E. G.

The System: Potassium Nitrate, Sodium Chloride, Water. J. Walter Leather and Jatindra Nath Mukerji (*Mem. Dept. Agric. India*, 1914, **3**, 177—204).—The equilibrium relations in the quaternary system formed by the reciprocal pairs of salts and water have been investigated by measurements of solubility at 20°, 30°, 40°, and 91°. For this purpose, preliminary measurements were made in respect of the four ternary systems: (1) potassium nitrate, sodium nitrate, water; (2) sodium nitrate, sodium chloride, water; (3) sodium chloride, potassium chloride, water; (4) potassium chloride, potassium nitrate, water. The data for the first ternary system show that each salt increases the solubility of the other, whereas in the three remaining systems each salt diminishes the solubility of the other.

In regard to the quaternary system, the conclusion is drawn that the system exhibits a change in character at about 30°. At temperatures above 31°, with potassium nitrate and sodium chloride in excess, potassium chloride separates out as a third solid phase, whereas below 28° sodium nitrate is found in place of potassium chloride as a third solid phase.

The solubility data for the several systems are recorded in tabular form.

H. M. D.

The Systems: (*A*) Water, Magnesium Carbonate, and Carbon Dioxide; (*B*) Water, Calcium Carbonate, Magnesium Carbonate, and Carbon Dioxide. J. Walter Leather and Jatindra Nath Sen (*Mem. Dept. Agric. India*, 1914, **3**, 205—234).—Measurements have been made of the solubility of magnesium carbonate ($MgCO_3$,$3H_2O$) in water saturated with carbon dioxide at 20°, 25°, 30°, 34°, and 39°, and at carbon dioxide pressures corresponding with 0·5 to 30·3% of carbon dioxide in the gas phase. It is found that the concentration of the magnesium carbonate and of the carbon dioxide in the solution can be represented by the formula $c^n=kp$, in which k and n are constants which vary with the temperature according to linear formulæ, and p is the percentage of carbon dioxide in the gas phase.

For a given partial pressure, the concentration of the magnesium carbonate and carbon dioxide in the solution is from five to fifteen times greater than that found in the case of calcium carbonate. In all cases, the ratio of $MgCO_3$: CO_2 indicates that the solutions contain only small quantities of carbon dioxide in excess of that required for the formation of magnesium hydrogen carbonate.

The more complex system *B* has only been submitted to a partial examination. The data show that calcium carbonate dissolves to only a very small extent in presence of magnesium carbonate. This behaviour is in accord with the relative stabilities of the respective hydrogen carbonates in aqueous solution.

Some experiments with dolomite show that this dissolves as such in aqueous solutions of carbon dioxide, but the solubility depends on factors other than that of the carbon dioxide concentration. In addition, it was found that dolomite is protected from the action of carbon dioxide to a large extent in presence of calcium carbonate, and completely in presence of magnesium carbonate. It was also observed that magnesium carbonate was precipitated to a slight extent when calcium carbonate was added to a solution of dolomite in aqueous carbon dioxide. No explanation can be offered which will account for this anomalous result.

The effect of the addition of magnesium carbonate to agricultural land is discussed. Since this may lead to the almost complete precipitation of calcium carbonate from the soil solution, it is possible to offer an explanation of the failure of crops which has been frequently observed after the application of magnesium carbonate to the soil in experiments on Loew's "lime–magnesia ratio."

H. M. D.

Mechanism of Molecular Action. A Contribution to the Kinetic Theory of Gases. T. CARLTON SUTTON (*Phil. Mag.*, 1914, [vi], **28**, 798—808).—By combination of the mass law with a thermodynamic relation obtained by Gibbs and Planck (compare Planck, "Thermodynamik," equation 204), it is shown that the velocity of the reversible reactions represented by the formula $\lambda_1 P_1 + \lambda_2 P_2 + \ldots \rightleftarrows \mu_1 Q_1 + \mu_2 Q_2 + \ldots$ can be expressed by

$$k\Pi[P]^{\lambda} . e^{-(A/\theta)} . \phi(\theta) \text{ and } k'\Pi[Q]^{\mu} . e^{-(A'/\theta)} . \phi(\theta),$$

in which θ is the absolute temperature and Π is the symbol of a product. The two expressions differ only in the values to be assigned to the constants k and k', A and A'. According to these expressions, the number of effective collisions varies with the temperature according to some function which involves $e^{-(A/\theta)}$. It is shown that the molecular mechanism which is consistent with the above expressions for the reaction velocity is limited to two alternatives. According to one of these, reacting molecules must collide with a relative velocity of approach which exceeds some particular value v, whilst according to the other, reaction is limited to those molecules which collide with a relative velocity of approach lying between v and $v + \delta v$.

The case of the unimolecular reaction is considered separately, and the fact that the influence of temperature in this case is represented by a function of the same exponential type suggests that the reaction in question is caused by the collision of atoms within the molecule, which are characterised by a relative velocity of approach in excess of a limiting value v, or by velocities within the limits given by v and $v + \delta v$.

H. M. D.

Action of Phenols and of Alcohols on Ethyl Diazoacetate. G. CALCAGNI (*Gazzetta*, 1914, **44**, ii, 447—455).—Bredig and Fraenkel (A., 1905, ii, 692; 1907, ii, 746) have shown that the hydrolysis of ethyl diazoacetate to nitrogen and ethyl glycollate

constitutes a very sensitive reaction for hydrogen ions. The author has employed this hydrolysis to measure the hydrogen-ion concentration in solutions of phenol, catechol, resorcinol, quinol, pyrogallol, phloroglucinol, mannitol, erythritol, glycerol, ethylene glycol, and ethyl alcohol. The results show that phenols function as weak acids, the strength of which increases with the number of hydroxyl groups, and depends on their positions. Aliphatic alcohols also dissociate, but to such a slight extent that the concentrations of the hydrogen ions are not sufficiently great to decompose the ethyl diazoacetate; measurements of the conductivity, however, show that the degree of the dissociation increases with the number of hydroxyl groups in the molecule.

Bredig and Fraenkel (*loc. cit.*) found that the ratio K_H of the velocity constant, K, to the concentration of the hydrogen ions, C_H, is almost constant, and has about the value 38·5 for all organic and inorganic, saturated and unsaturated, weak and strong, acids in aqueous solution. For the phenols, the velocity constants are at first low, and only slowly assume their constant values. For phenol, $K=0·000143$ and $C_H=0·000003714$; for catechol, $K=0·000369$ and $C_H=0·000009584$; and for pyrogallol, $K=0·00130$ and $C_H=0·00003377$. The dissociation constants calculated from the conductivities of solutions of these compounds of different concentrations are not very concordant, but increase slightly in passing from the monohydric to the trihydric phenols, this behaviour corresponding with the catalytic activities and also with the neutralisation curves traced by Thiel and Römer (A., 1908, i, 787). T. H. P.

Velocity of Crystallisation of Undercooled Water. James H. Walton, jun. and Roy C. Judd (*J. Physical Chem.*, 1914, **18**, 722—728).—The velocity of crystallisation of water has been determined at temperatures down to −9°. The experiments were carried out by filling a tube, 1 metre long and 7 mm. internal diameter, and 2·5 mm. wall, with conductivity water. The free ends of the column of water were covered with a layer of paraffin oil, and the whole cooled in a specially constructed thermostat (this vol., ii, 12). When the water had cooled to the temperature of the bath, crystallisation was induced by scratching the inside wall of the tube below the paraffin layer, and the time required for the crystallisation to traverse the whole length of the tube noted by means of a stop-watch. The following values, in cm. per minute, were obtained at the different temperatures: −2°, 31·6; −3·61°, 48·4; −4·67°, 71·4; −5·86°, 107·1; −6·18°, 114·7; −7·10°, 266·7; −7·50°, 308·0; −8·19°, 415·2; −8·38°, 513·0; and −9·07°, 684.0. Measurements below −9·07° could not be made owing to spontaneous crystallisation taking place before the water had attained the desired temperature. The maximum velocity of crystallisation lies at a temperature below −9·07° and was not obtained. Several experiments on the influence of the thickness of the walls of the tubes were carried out.

J. F. S.

Present Aspect of the Hypothesis of Compressible Atoms. Theodore W. Richards (*J. Amer. Chem. Soc.*, 1914, **36**, 2417—2439).—An account is given of the author's hypothesis of compressible atoms and its applications to the properties of gases, liquids, and solids (compare T., 1911, **99**, 1201). A bibliography of the subject is appended. E. G.

Chemically Resistant Glass Lacquer. Paul J. Fox (*J. Physical Chem.*, **1914**, **18**, 759—761).—The author describes a lacquer for coating glass, which is prepared by pouring 100 c.c. of carbon disulphide over 15 grams of pure unvulcanised rubber. The mixture is left for several hours until homogeneous, then 30 grams of white ceresin cut into small pieces are added, and a further quantity of 100 c.c. of carbon disulphide. In this way a liquid mixture of the consistency of glycerol is produced. The vessel to be treated is cleaned and then rinsed with alcohol and drained. It is then half filled with the solution and shaken and immediately drained, and allowed to dry for four to five hours. Chloroform or carbon tetrachloride may be used instead of carbon disulphide, but in these cases the lacquer is applied hot. If the coating breaks in one place it may be covered with a little of the solution, there being no necessity to remove the whole coating. The lacquer is not affected by fairly strong hydrogen fluoride. J. F. S.

Inorganic Chemistry.

Isolation of Oxygen from Air. L. BERGFELD (Brit. Pat. 21211 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 831).—The vapour of nitric acid is passed over heated sulphuric acid to form oxygen, water, and nitrosylsulphuric acid. The last substance is treated with water to form sulphuric acid and nitrogen trioxide, the latter being then reconverted into nitric acid by means of water and atmospheric oxygen. The equations are: (i) $4HNO_3=4NO_2+2H_2O+O_2$; (ii) $4H_2SO_4+4NO_2=4H(NO)SO_4+2H_2O+O_2$; (iii) $2H(NO)SO_4 + H_2O = 2H_2SO_4 + N_2O_3$; (iv) $N_2O_3+O_2+H_2O = 2HNO_3$.

The cycle of operations is completed continuously in a system of refractory and acid-proof tubes acting as heat interchangers on the counter-current principle, the tubes being preferably packed with quartz grains or the like, which offer resistance to the flow of liquids and facilitate the interchange of heat. C. S.

Preparation of Thionyl Chloride. FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (Brit. Pat. 27830 of 1913; from *J. Soc. Chem. Ind.*, 1914, **33**, 830).—Thionyl chloride is obtained by the reaction of sulphur or sulphur chloride with chlorine and chloro-

sulphonic acid, or of sulphur dichloride with chlorosulphonic acid, with or without the addition of a catalyst such as antimony trichloride or mercuric chloride. C. S.

Preparation of Thionyl Chloride. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 275378; from *J. Soc. Chem. Ind.*, 1914, **33**, 831).—Thionyl chloride is produced by the interaction of sulphur trioxide and sulphur dichloride at the ordinary temperature and pressure in presence of suitable catalysts, such as antimony trichloride, mercuric chloride, or chlorides of other heavy metals. T. H. P.

Preparation of Hydrazoic Acid or Azides. H. STAUDINGER (D.R.-P. 273667; from *J. Soc. Chem. Ind.*, 1914, **33**, 693).—When hydrazine hydrate or a hydrazine salt is treated with the nitrosoamine of a secondary amine, such as diphenylamine, in alcoholic solution and in presence of alkali hydroxide or carbonate, the following reaction takes place, slowly in the cold, but more rapidly on heating: $NPh_2{\cdot}NO + N_2H_4 + NaOH = NHPh_2 + N_3Na + 2H_2O$. T. H. P.

Thermal Dehydration of Stilbite, Thaumasite, and the Hydrates of Magnesium Sulphate and of Copper Sulphate. H. E. MERWIN (*J. Washington Acad. Sci.*, 1914, **4**, 494—496).—Small quantities of the substances mentioned above were heated between the walls of thin glass tubes in an oil-bath at a series of temperatures, and the rate at which the water was expelled at the various points was determined. Copper sulphate is shown to lose first two molecules of water, then two more, and finally the last at a much higher temperature. Stilbite loses 17·6% of water without any evidence being obtained of a break in the dehydration curve. Magnesium sulphate gives four maxima in the rate of evolution of water, corresponding with the expulsion of $4H_2O$ and three single molecules. Thaumasite,

$$CaSO_4,CaCO_3,CaSiO_3,15H_2O,$$

loses first of all 14 molecules of water, the last one being held much more firmly. J. F. S.

Hydrolysis of Zinc Chloride. ALFREDO SORDELLI (*Anal. Soc. Quim. Argentina*, 1914, **2**, 97—112).—The addition of water to concentrated solutions of zinc chloride does not cause any separation of the basic chloride, $2ZnCl_2,11ZnO$; the latter is formed when the solution contains an excess of zinc oxide. The precipitation is exothermic. The hydrolysis constant, as determined by means of methyl acetate or sucrose, is small, even at 100°. G. D. L.

Complex and Basic Lead Salts. Cause of the Solubility of Lead Sulphate in Ammonium Acetate. C. BLOMBERG (*Chem. Weekblad*, 1914, **11**, 1030—1034).—From the results of determinations of the freezing point and electrical conductivity

of solutions of lead acetate, the author draws the conclusion that the solubility of lead sulphate in such solutions is due to the formation of either complex or basic salts. A. J. W.

Supposed Crystalline Compound of Ferrous Chloride and Nitric Oxide. I. Bellucci (*Gazzetta*, 1914, ii, 384—389).—The experimental conditions employed by Thomas (A., 1896, ii, 26) give a yellow, microcrystalline mixture of ferric chloride with a small proportion of nitric acid, and not the compound, $FeCl_2,NO$, which has not yet been prepared. Manchot's ferronitricoxide phosphate (compare A., 1914, ii, 567) is, therefore, the only compound of the type $[Fe(NO)]X_2$ as yet known. T. H. P.

Ternary Alloys of Nickel–Copper–Lead. N. Parravano [with C. Mazzetti] (*Gazzetta*, 1914, **44**, ii, 375—384).—The author has traced the fusion diagram of these alloys, which exhibit partial miscibility in the liquid state. Nickel–copper alloys form a continuous series of mixed crystals with melting points falling continuously from that of nickel to that of lead. With lead–nickel alloys, the melting-point curve falls from 1451°, at which nickel melts, to 1338°, the temperature of the invariant equilibrium between a solid and two liquids, one containing about 30% and the other about 85% of lead; subsequently the curve falls rapidly to a eutectic, which consists of practically pure lead, and solidifies at 327°. Similar behaviour is exhibited by copper–lead alloys, the limits of miscibility being about 36—85% of lead.

Given the existence of two miscibility gaps in the binary alloys, two simple hypotheses present themselves with reference to the manner in which these gaps are continued into the triangular diagram of the ternary alloys: (1) the two gaps may undergo restriction, each exhibiting a critical point; (2) the two gaps may be continued one into the other, giving rise to a whole zone of liquid gap, which interrupts the continuity of the fusion surface and divides the latter into two clearly distinct parts. Experiment shows that case (2) is verified with nickel–copper–lead alloys, this result being in accord with that furnished micrographically.

The results indicate the following method of removing nickel and copper from lead. The ternary eutectic virtually coincides with the lead vertex of the triangular diagram, so that mixtures in the neighbourhood of lead, at temperatures intermediate to those corresponding with the beginning and end of solidification, consist of a solid part containing the greater part of the nickel and copper in the form of mixed crystals and of almost pure liquid lead; the mixed copper–nickel crystals are lighter than the liquid and can be readily removed. Since the quantity of crystals gradually increases as the temperature is lowered from that corresponding with the commencement of the crystallisation to that of the eutectic plane, the temperature of the bath should be as low as possible. The rapid fall of the surface of fusion in the neighbourhood of the lead point ensures the success of the operation, since it allows of moderately wide variations in the temper-

ature of the bath without rendering possible the failure of the separation. T. H. P.

Artificial Macles of Tin. P. GAUBERT (*Compt. rend.*, 1914, **159**, 680—682. Compare Ewing and Rosenhain, *Phil. Trans.*, 1900, **193**, [*A*], 353; 1901, **195**, [*A*], 279).—A study of the conditions governing the formation of bands of twin crystals in tin. The sheets of tin are prepared of the required thickness by melting and casting them between two smooth, well-polished plates of glass. On suddenly piercing such a sheet of tin with a needle there are produced (1) on the side remote from where the needle entered, a cross in relief, the branches being very broad and equal or unequal, according to the crystalline orientation of the sheet of tin; (2) two or three series of brilliant, parallel bands, about 0·5 mm. broad, and extending from the point of penetration to the edges of the crystal. Their exterior face, at first in the plane of the sheet, makes an angle of several degrees with it. The crystals of tin do not always arrange themselves in the same manner with respect to the sheet of glass, and the angle which the two or three series of bands make between them is variable. Some sheets of tin give bands making an angle of 87°, others give two kinds of bands making an angle of 71°, whilst others give three series of bands of which the angles are 45°, 71°, and 64°.

The folding or twisting of a sheet of tin results in the formation of twinned bands. The "cracking" of tin is probably due to the formation of these macles. W. G.

Electrolysis of Antimony Chloride in Presence of Colloids. ARRIGO MAZZUCCHELLI (*Gazzetta*, 1914, **44**, ii, 404—419).—The presence of antimony chloride in electrolytic antimony cannot be prevented by carrying out the electrolysis of the chloride in a solution containing a colloid. Many colloids, including resorcinol, tannin, molybdic acid, starch, and gum, have no influence on the aspect and properties of the metallic deposit, but the presence of proteins, especially of gelatin, results in the separation of antimony which exhibits increased lustre and fragility and is explosive towards heat, but only slightly so towards shock. Quinine, with which antimony chloride forms a double chloride, sparingly soluble in concentrated hydrochloric acid, has an effect similar to that of the proteins; the cationic function of the alkaloid appears to favour its absorption by the metal. Lowering of the temperature at which the electrolysis takes place renders the metallic deposit pitted and less adherent, owing to increase in the cathodic evolution of hydrogen.

From these results the conclusion is drawn that in explosive electrolytic antimony, the metal and the chloride form a true, not a colloidal, solution. Such a solution is formed by antimony with its chloride, bromide, or iodide, but not with the fluoride. T. H. P.

Mineralogical Chemistry.

The Calculation and Comparison of Mineral Analyses. C. E. VAN ORSTRAND and FRED. E. WRIGHT (*J. Washington Acad. Sci.*, 1914, **4**, 514—525).—A mathematical discussion and criticism of the papers by Schaller and Wells (*ibid.*, 1913, **3**, 97, 416) on the calculation of mineral formulæ and the interpretation of mineral analyses. In all cases the method of least squares is involved. Several equations and formulæ are given for the computation of the probable errors and the adjustment of the data. L. J. S.

Identity of Empressite with Muthmannite. WALDEMAR T. SCHALLER (*J. Washington Acad. Sci.*, 1914, **4**, 497—499).—The two minerals, empressite (Bradley, A., 1914, ii, 737) and muthmannite (Zambonini, A., 1911, ii, 734), are considered by the author to be really the same substance. The physical characteristics are very similar, the only difference being that whilst empressite is AgTe and contains no gold, muthmannite contains considerable quantities of gold, and is expressed by the formula (AgAu)Te. The quantity of gold is, however, always less, molecularly, than the silver; the author, therefore, expresses the opinion that empressite is only pure muthmannite, and could be more accurately named muthmannite, whilst the original mineral should be named auric muthmannite. J. F. S.

Analytical Chemistry.

Symbolical Representation of Analytical Operations. L. GOWING-SCOPES (*Chem. News*, 1914, **110**, 247—250).—A list of some ninety symbols for representing analytical operations is given; their use is indicated by a number of examples. W. P. S.

Dihydroxydistyryl Ketone or Lygosin, a New Indicator. ARON FERENEZ (*Ann. Chim. anal.*, 1914, **19**, 232; from *Pharm. Post.*, 1913, 521).—When 2 mols. of salicylaldehyde and 1 mol. of acetone in alcoholic solution are treated with concentrated sodium hydroxide solution, condensation takes place with the formation of a salt which may be crystallised from alcohol; this salt, on treatment with an acid, yields *o*-dihydroxydistyryl ketone, a substance giving an orange-red coloration with alkalis and a turbid opalescence with acid solutions. The indicator may be used in the form of a 1% alcoholic solution; it is stated to be as sensitive as phenolphthalein and may be employed in the titration of ammonia. W. P. S.

Methyl-red as an Indicator. R. T. THOMSON (*Analyst*, 1914, **39**, 518—519).—This indicator is especially useful in the titration of ammonia and weak bases, such as quinine (compare A., 1909, ii, 90); its colour change is sharper than that of methyl-orange and its sensitiveness is but little affected by the presence of neutral salts, such as sodium chloride or sulphate. It must not be assumed that methyl-red can be substituted for methyl-orange or that it will act similarly to the latter; methyl-red is affected by dissolved carbon dioxide, and when used as the indicator in the titration of carbonates, the solution must be boiled after each addition of acid, in order to expel the liberated carbon dioxide. Methyl-red, in this respect, most closely resembles litmus (compare also T., 1910, **97**, 2477). W. P. S.

Qualitative Test for Water by the Use of the Acetylene-Cuprous Chloride Reaction. E. R. WEAVER (*J. Amer. Chem. Soc.*, 1914, **36**, 2462—2468).—The presence of water in a substance can be readily detected by bringing it into contact with calcium carbide and a solvent for acetylene, and then decanting or distilling the resulting solution into an ammoniacal solution of cuprous chloride. Most of the usual organic solvents, if carefully dried, are suitable for this purpose. The method is applicable to a great variety of substances and especially to the volatile organic compounds. The only compounds which interfere with the test are the stronger acids and substances, such as hydrogen sulphide, which precipitate cuprous salts from solution. The test is sensitive to less than 0·1 mg. of water. E. G.

Rapid Methods of Estimating Water in Crude Petroleum, Oil-Fuel, and Similar Substances. HERBERT S. SHREWSBURY (*Analyst*, 1914, **39**, 529—531).—A simple method is described for estimating the water by distillation. One hundred c.c. of the oil and a few pieces of pumice-stone are placed in a distillation flask, which is so supported that its side-tube passes vertically downwards into a graduated cylinder surrounded by cold water. After the neck and surface of the flask (uncovered by the oil) have been heated cautiously with a flame, the oil itself is heated until all the water and a few c.c. of oil have distilled over into the cylinder, and the volume of the water is read. Another method depends on the extraction of the water from oil-fuel by glacial acetic acid and on the alteration of the turbidity temperature of the acid with a standard oil, caused by the presence of the water. The turbidity temperature of the acetic acid with the oil (equal volumes of arachis and cocoanut oils) is ascertained; 10 c.c. of the standardised acid and 10 c.c. of the oil-fuel are then shaken together, the acid layer is separated, filtered, and 2 c.c. of the filtrate are heated with 2 c.c. of the standard oil until the mixture is clear, and its turbidity temperature determined. Standards must be prepared by adding known quantities of water to the acetic acid. A correction is necessary for the effect on the turbidity temperature of substances, other than water, dissolved from the oil-fuel;

this is obtained by drying a portion of the oil-fuel by heating it in an open basin, and then shaking 2 c.c. of it with glacial acetic acid as described. When the oil-fuel contains more than 2·5% of water, the acetic acid extract must be diluted with acetic acid, exactly the same dilution being made in the case of the extract giving the figure for the correction. Both methods can probably be used for the estimation of water in substances such as butter, lard, and other fats and oils. W. P. S.

Examination of Sulphur Chloride. F. FRANK and E. MARCKWALD (*Gummi-Zeit.*, 1914, **28**, 1580—1581; from *J. Soc. Chem. Ind.*, 1914, **33**, 749).—Whilst pure sulphur chloride has D^{15} 1·684, samples having D^{15} 1·680 to 1·690 may be considered as satisfactory. When 105 c.c. are distilled, using a standard flask and condenser (of which minute details are given), 95 c.c. should distil within 4°, the first 5 c.c. being rejected. The sample should contain at least 98·8% of S_2Cl_2, calculated on the chlorine content estimated by the following method: From 10 to 15 c.c. of nitric acid (D 1·5) and a quantity of silver nitrate sufficient for the reaction are introduced into a small pressure flask having a ground-in stopper secured by a lever. A small weighing bottle containing from 0·2 to 0·5 gram of the sample is then dropped into the flask, this is shaken until all the sulphur chloride has disappeared, and is then heated for thirty minutes on a water-bath, cooled, and opened. The precipitate is collected, dissolved in ammonia, re-precipitated, again collected and weighed. The method yields trustworthy results higher than those obtained by the older process. W. P. S.

Modified Kjeldahl Flask for Estimating Soil Nitrogen. H. A. NOYES (*J. Amer. Chem. Soc.*, 1914, **36**, 2541—2542).—As the amount of nitrogen in ordinary soil is small, a large sample must be employed for its estimation, and this usually necessitates the transference of the solution from the digestion flask to another flask for distillation to avoid bumping. In order to obviate this transference, a modified Kjeldahl flask may be used, which has a capacity of about 700 c.c. and differs from the ordinary form in being egg-shaped. The pointed bottom of the flask prevents the solid matter from settling during the heating, and frothing does not occur, as the bubbles are broken against the sides of the flask. The flask has proved very satisfactory in practice. E. G.

Preparation of Reduced Strychnine Reagent for the Colorimetric Estimation of Nitrates in Water. G. DENIGÈS (*Ann. Chim. anal.*, 1914, **19**, 221—222; from *Bull. Soc. pharm. Bordeaux*, 1914. Compare A., 1911, ii, 655, 673).—The zinc amalgam used is obtained by immersing 50 grams of zinc foil, cut into small strips, in a mixture of 50 c.c. of water and 20 c.c. of hydrochloric acid (D 1·18), and then adding 10 c.c. of 4% mercuric chloride solution; after two minutes' contact, the strips are washed with water, placed on a sheet of filter paper until dry, and then

stored in a closed bottle. The reagent itself is prepared immediately before use as described (*loc. cit.*). The red coloration, produced by the action of nitrates on the reagent in the presence of sulphuric acid, attains its full intensity only after the reacting mixture has been heated on a boiling water-bath for five minutes. W. P. S.

Estimation of Phosphorus in Phosphor-Bronze. E. W. HAGMAIER (*Met. and Chem. Eng.*, 1914, **12**, 524—525; from *J. Soc. Chem. Ind.*, 1914, **33**, 923—924).—One gram of the bronze is dissolved in a mixture of 10 c.c. of hydrochloric acid and 5 c.c. of nitric acid, the solution is diluted with 150 c.c. of hot water, 10 c.c. of a solution containing 1 gram of cerium chloride in 25 c.c. of hydrochloric acid and 200 c.c. of water are added, and ammonia is run in slowly from a burette until a greenish-blue coloration appears. Four c.c. of acetic acid are now added, and the mixture is boiled for ten minutes. After settling, the clear liquid is siphoned off, the precipitate washed by decantation with 100 c.c. of hot water (added in about six successive portions), and dissolved by heating with 15 c.c. of nitric acid and 3 c.c. of hydrochloric acid. When cold, the solution is treated with 5 c.c. of ammonia (1 : 1), and the phosphoric acid precipitated in the usual way with ammonium molybdate. W. P. S.

Estimation of Boric Acid and its Compounds in Extract of Tomatoes and Other Preserved Foods. NICOLÁS CAMUS (*Anal. Soc. Quim. Argentina*, 1914, **2**, 123—130).—After ashing, the residue, from which all the carbon need not be burnt off, is moistened with strong hydrochloric acid, and the boric acid extracted with acetone. After evaporation of the solvent, the residue is dissolved in about 3 c.c. of very dilute hydrochloric acid, and the boric acid recognised by means of turmeric paper. By standardising the conditions, size of paper, strength of turmeric, etc., it is possible to obtain approximately quantitative values. G. D. L.

Estimation of Cadmium in Zinc. W. COOPER (*Chem. News*, 1914, **110**, 250—251).—Five grams of the sample are dissolved in a cold mixture of 150 c.c. of water and 7 c.c. of sulphuric acid, and the solution is decanted into a flask, any undissolved residue being washed with a small quantity of water. Twenty c.c. of dilute sulphuric acid are then added to the solution, the mixture is diluted to 250 c.c., treated with hydrogen sulphide for twenty minutes, and, after two hours, the precipitated cadmium and zinc sulphides are collected on a filter. The sulphides are now dissolved in hydrochloric acid containing bromine, 5 c.c. of sulphuric acid are added, and the mixture is heated until fumes of sulphuric acid are given off. This residual solution is diluted to 50 c.c., any lead sulphate is separated, and the precipitation with hydrogen sulphide and treatment with sulphuric acid are repeated. The solution is once more treated with hydrogen sulphide, the cadmium sulphide is collected on a weighed filter, washed, dried at 100°, and weighed. W. P. S.

Iodate Method for the Estimation of Copper. W. W. Brostrom (*Eng. and Min. J.*, 1914, **98**, 215—216; from *J. Soc. Chem. Ind.*, 1914, **33**, 891).—The copper is reduced with sodium sulphite solution in the presence of hydrochloric acid, and precipitated with potassium thiocyanate. The precipitate is washed, decomposed with hydrochloric acid in the presence of a small quantity of carbon tetrachloride, and the solution titrated with potassium iodate solution until the red colour produced at first is discharged. Results are given showing that the method is trustworthy. W. P. S.

Estimation of Cuprous and Cupric Sulphides in Mixtures of One Another. Eugen Posnjak (*J. Amer. Chem. Soc.*, 1914, **36**, 2475—2479).—During an investigation of copper sulphide minerals, it was desired to estimate cuprous and cupric sulphides in presence of one another. A method has therefore been devised which depends on the difference in the behaviour of the sulphides towards silver nitrate as shown by the equations $Cu_2S + 4AgNO_3 = Ag_2S + 2Ag + 2Cu(NO_3)_2$ and $CuS + 2AgNO_3 = Ag_2S + Cu(NO_3)_2$.

In order to carry out an estimation, the substance must be fine enough to pass through a sieve of 80 meshes per cm.. About 0·4—0·5 gram of the material is treated with 50 c.c. of 5% silver nitrate solution, which is added gradually with vigorous stirring. To complete the reaction, the mixture is heated on the steam-bath for three hours, and stirred vigorously at short intervals. The precipitate is collected and washed, and then treated two or three times with 6% ferric nitrate solution at 70° to extract the silver. The extract is filtered, and the residue washed with hot water. Nitric acid is added to the filtrate until it becomes colourless, and the silver is then precipitated and weighed as the chloride. The amount of cuprous sulphide is calculated from the silver found, whilst the cupric sulphide is calculated from the difference between the silver in the silver sulphide and that precipitated in the metallic form.

The method has been found to be accurate within 1·5% for the analysis of mixtures of the sulphides in any proportions. E. G.

Electrolytic Estimation of Nickel. W. Judson Marsh (*J. Physical Chem.*, 1914, **18**, 705—716).—It is shown that when nickel is estimated electrolytically by deposition from solutions containing an excess of ammonium oxalate, the weight of the deposit is always too high, owing to the presence of carbonaceous material. The present paper deals with experiments made with the object of improving the process. The nickel deposit is shown to contain nickel carbide, which is supposed to be formed by the action of acetylene on the freshly deposited metal. The acetylene is produced by the cathodic reduction of carbon monoxide and carbon dioxide formed at the anode. Attempts were made to reduce the amount of carbon dioxide formed by adding reducing agents to the solution, such as hydrazine sulphate, hydroxylamine sulphite, sodium nitrite, and sodium sulphite. Of these substances,

the first, only, produced a noticeable effect, inasmuch as it caused the deposit to be much darker, probably due to the formation of nickel sulphide. This conclusion is rendered likely because when a nickel solution was electrolysed in the presence of ammonium carbonate and sodium sulphite, a flocculent precipitate of nickel sulphide was produced and hydrogen sulphide was evolved. Having failed to improve the oxalate method of estimation, the author has investigated a number of other methods, and comes to the conclusion that the electrolysis of the double ammonium sulphate solutions of nickel gives the best results. A solution of nickel sulphate containing about 0·2 gram of nickel in 200 c.c. is mixed with 15—20 c.c. of ammonium hydroxide solution (D 0·96) and 5 grams of ammonium sulphate. The electrolysis is effected between an anode of platinum gauze, 6 cm. × 4·5 cm., and a cathode of copper gauze, made in the form of a cylinder, 5 cm. high and 3 cm. diameter. The cathode is rotated at 550—650 revolutions per minute. The electrolysis is carried out at ordinary temperature with a current of 0·8 ampere and an *E.M.F.* of 3·5 volts, and requires about twenty-five minutes. It is essential that nitrates and chlorides should be absent. J. F. S.

Modifications of the Reduction Test for Tungstic Acid. G. Torossian (*Amer. J. Sci.*, 1914, [iv], **38**, 537—538).—When powdered tungstic acid is placed on aluminium foil and moistened with a drop of dilute hydrochloric acid, a blue coloration is obtained; the reaction is also given by tungstic acid after fusion with sodium carbonate, and the presence of ferric oxide, copper oxide, lead oxide, sulphur, calcium fluoride, or sodium nitrate does not interfere with the test. W. P. S.

Assay of Crude Platinum. M. Schwitter (*Eng. and Min. J.*, 1914, **97**, 1249—1250; from *J. Soc. Chem. Ind.*, 1914, **33**, 751).—Twenty grams of the nuggets are digested with 200 c.c. of aqua regia ($1HNO_3 : 3HCl$) on a water-bath for one hour, and then boiled for two hours. The solution is decanted and again boiled to dissolve any finely divided metal in suspension. The aqua regia treatment is repeated on the residue, the mixture is diluted, and allowed to settle. After about eighteen hours, the clear solution is decanted, and the last portion filtered into a litre flask, the filter being washed until colourless. *Osmiridium.*—The residue from the acid treatment is scorified with 10—15 grams of test lead and enough litharge to fill the scorifier. The button is cleaned with as little hammering as possible, and dissolved in dilute nitric acid (1 : 3); the solution containing the lead is filtered, the filter washed free from lead, and dried. The osmiridium is separated as completely as possible from the paper, the latter is burned, and the ash added to the metal, which is weighed. *Platinum.*—Twenty-five c.c. of the filtrate are evaporated to dryness, the residue heated for one hour, with occasional stirring, with 5 c.c. of hydrochloric acid (1 : 9), 20 c.c. of water, and 8 grams of ammonium chloride, and then set aside for eighteen hours; the

platinichloride is collected, washed with 20% ammonium chloride solution, and ignited in an annealing cup. The metal contains most of the iridium; the quantity of the latter, if not more than 5%, can be judged with sufficient accuracy from the colour of the platinichloride, 0·2% of iridium sufficing to impart a decided red tint. *Gold.*—The filtrate from the platinichloride is treated with 5 grams of ferrous sulphate, the gold collected, and ignited. *Palladium.*—The filtrate from the gold is treated with one-fifth of its volume of hydrochloric acid, and 10% potassium iodide solution is added, five drops at a time, until no further quantity of black precipitate (PdI_2) forms. The mixture is boiled, cooled, the precipitate collected, washed with dilute hydrochloric acid (1 : 4) until free from iron, ignited in a porcelain crucible, then heated with a few drops of formic acid to reduce any oxide, dried, and weighed. *Rhodium.*—The filtrate from the palladium is reduced, while hot, with zinc, and the metallic precipitate is digested for ten minutes on a water-bath with 25 c.c. of dilute nitric acid (1 : 3); the residue is ignited, reduced in hydrogen, and weighed as rhodium; it contains the last traces of iridium. W. P. S.

Detection and Estimation of Combustible Gases in Mineral Waters. ENRIQUE HAUSER (*Anal. Fis. Quim.*, 1914, **12**, 155—163, 256—259. Compare A., 1914, ii, 285).—A minute description of the eudiometer devised by the author for the estimation of combustible gases in water, and of the mode of operating it. The gas is ignited electrically in the eudiometer, and the products are analysed by means of ordinary absorption pipettes. The solubility of methane varies according to the nature of the saline solution. A. J. W.

Rapid Method for the Detection and Estimation of Solid Hydrocarbons Mixed with Fatty Acids. G. VERONA-RINATI (*Ann. Chim. Applicata*, 1914, **2**, 201—202).—This method is carried out as follows. By means of a burette, 7 c.c. of dry α-dichlorohydrin, b. p. 174°, are measured into a glass tube having a diameter of about 10 mm. and a capacity of about 15 c.c., and graduated to read easily to 0·1 c.c. To this are added 1·2 c.c. of water and 1·43 grams of the substance to be tested. The tube is closed tightly by means of a cork, and immersed in a beaker of water maintained at 65°, being removed and well shaken from time to time. When the liquefied mass is no longer diffused uniformly throughout the whole of the liquid, the tube is left at rest for ten minutes, and the volume of the undissolved part collected at the top is read; this reading is repeated after further heating and shaking. Each 0·1 c.c. of this volume corresponds with 5% of fatty matter of mineral origin in the original substance.

In order to ascertain whether such mineral fat consists of cerasin or paraffin or a mixture of these, about 2—3 grams of the original material are treated in a test-tube with the aqueous α-dichlorohydrin until the fatty acids are completely dissolved. The tube is then allowed to cool until the undissolved portion

becomes consolidated at the top, whilst the fatty acids remain in solution in the liquid underneath. The solid mass is removed and pressed between filter papers to free it from the solvent; 0·2 gram of it is heated, in a test-tube over a naked flame, with 10 c.c. of anhydrous α-dichlorohydrin, and the temperature is determined at which the dissolved hydrocarbon begins to separate again and render the liquid turbid. When this hydrocarbon consists solely of paraffin, this temperature never exceeds 92° (88—92°), whilst with cerasin it is never below 112° (112—115°). With a mixture of paraffin and cerasin, the temperature of separation lies between 92° and 112°, and its value indicates which of the two predominates in the mixture. T. H. P.

Estimation of Sucrose and Lactose in Condensed Milk by means of Acid Mercuric Nitrate. CECIL REVIS and GEORGE A. PAYNE (*Analyst*, 1914, **39**, 476—479).—The acid mercuric nitrate solution employed is prepared by dissolving mercuric oxide in twice its weight of nitric acid, D 1·42, and diluting the solution to five times its volume with water. A quantity of 65·085 grams of condensed milk is dissolved in about 220 c.c. of water, heated in a boiling water-bath for about five minutes (or kept cold for sixteen hours), and then diluted to 250 c.c. at 15°. One hundred c.c. of this solution are transferred to a 100 c.c. cylinder, 10 c.c. of the mercuric nitrate solution are added, the mixture is shaken for thirty seconds, filtered after five minutes, and the filtrate is polarised at 20°. Twenty-five c.c. of the filtrate are then placed in a 50 c.c. stoppered flask, the flask and its contents are weighed, heated in a boiling water-bath for eight minutes, cooled, the weight is adjusted, and the solution polarised. The readings observed are corrected for the increase in volume due to the added reagent, less the volume of the fat and protein precipitated; this correction (C) will be:

$$C = 10 - [(F \times 1{\cdot}11) + (P \times 0{\cdot}82)/100 \times 26{\cdot}034] \text{ c.c.},$$

and the readings are multiplied by $(100 + C)$. Then sucrose $\% = (D - I)100/(R_C - t/2)$ and lactose $\% = (D - S) \times R_L \times 100/26{\cdot}034$, where D and I are the corrected direct and invert readings, R_C and R_L the inversion and lactose factors, and t the temperature of the invert reading. The factors R_C and R_L were found to be 141·71 and 0·3086 respectively; these figures are the results of actual experiment with sugar solutions of the concentration met with in the case of condensed milks, the authors having ascertained that acid mercuric nitrate has an inverting action on sucrose, and that it slightly raises the rotation of lactose. When the milk is clarified with phosphotungstic acid, the factors are found to be 142·55 and 0·3165, figures which agree with those recorded by other observers (compare A., 1907, ii, 586). W. P. S.

Flour. I. Acidity of Flour. II. Natural and Artificial Bleaching of Flour. III. Sulphates and Lime in Flour. R. T. THOMSON (*Analyst*, 1914, **39**, 519—527).—The aqueous extract of flour is acid to phenolphthalein, neutral to methyl-red,

and alkaline to methyl-orange. The acidity indicated by phenolphthalein is not due to the presence of lactic acid, since this acid is also indicated by methyl-red, and it is doubtful whether lactic acid is the acid produced when flour becomes "sour." There is no support for the usual statement that ordinary flour is acid in reaction. The author gives the results of experiments showing that artificial bleaching of flour by nitrogen peroxide does not have the same effect as natural bleaching, that is, by exposure to the atmosphere. Although flour absorbs nitrogen oxides from the air, the bleaching effect in this case is due to other causes, probably oxidation assisted by moisture and light. For the estimation of sulphates in flour, it is recommended that 20 grams of the flour should be mixed with 250 c.c. of water containing 15 c.c. of hydrochloric acid, D 1·16, and then heated until the starch is liquefied. The mixture is cooled, filtered, and the sulphates are precipitated in the filtrate by the addition of barium chloride. First-grade flour was found to contain 0·011% of SO_3 and 0·015% of CaO, whilst "common-thirds" yielded 0·061% of SO_3 and 0·102% of CaO (compare A., 1914, ii, 816). W. P. S.

Utz's Modification of Halphen's Reagent for Cottonseed Oil. ENRICO GASTALDI (*Ann. Chim. Applicata*, 1914, **2**, 203—207).—At no temperature does Utz's reaction (compare A., 1914, ii, 591) give the same coloration with cottonseed oil as Halphen's reagent, and as it is exhibited at 250—260°, at which temperature Halphen's test fails, it cannot be regarded as a modification of the latter. At a temperature exceeding 160°, which is usually surpassed in Utz's reaction, oleic, palmitic, or stearic acid gives a coloration similar to that obtained with cottonseed oil. This reaction cannot, therefore, be regarded as characteristic for cottonseed oil.

The author's modification of this test (compare A., 1912, ii, 1108) may be carried out very rapidly, and reveals the presence of small proportions of cottonseed oil, in the following manner: five to six drops of a 1% solution of sulphur in carbon disulphide and three to four drops of pyridine are added to 5 c.c. of the oil or fat, and the liquid heated directly over a flame for four to five minutes, care being taken that the temperature does not exceed 140°. T. H. P.

The Freezing Point of Milk. J. BROWNLIE HENDERSON and L. A. MESTON (*Chem. News*, 1914, **110**, 259—261, 275, 283—284; from *Proc. Roy. Soc., Queensland*, **24**, 165).—The freezing point of fresh, mixed milk from a herd of cows varies from −0·55° to −0·56°, the average being −0·555°. The constancy of the freezing point affords a means of detecting the presence of added water in milk, since a rise of 0·005° indicates the presence of about 1% of water. The freezing point is not, however, a measure of the proportion of total solids or of non-fatty solids in the milk. As the milk becomes acid, the freezing point is lowered, but the authors are not yet in a position to state whether any definite relation exists between the depression of the freezing point and

the increase of acidity. Tables are given showing c.c. of added water per litre to milk corresponding with temperatures ranging from $-0{\cdot}55°$ to $-0{\cdot}351°$ for differences of $0{\cdot}001°$, and the method of determining the freezing point is described in detail. W. P. S.

[Determination of the] Freezing Point of Milk. G. A. STUTTERHEIM (*Pharm. Weekblad*, 1914, **51**, 1311—1313).—A description of a modified form of Beckmann apparatus for the determination of the freezing point of milk (compare A., 1914, ii, 169, 304). A. J. W.

Estimation of the Cineole (Eucalyptol) Content of Eucalyptus Oils. HENRY G. A. HARDING (*Analyst*, 1914, **39**, 475—476).—The resorcinol method (compare A., 1908, ii, 233) for the estimation of cineole is untrustworthy when applied directly to eucalyptus oil, but better results are obtained by using the fraction of the oil, b. p. 170—190°, for the test. Even then the results tend to be too high, especially in the case of oils containing more than 50% of cineole. Turpentine has been suggested as a diluent, but, since it contains substances which are absorbed by resorcinol, only that portion should be used which distils between 156° and 160°. One hundred c.c. of the eucalyptus oil under examination are distilled, the fraction distilling between 170° and 190° is collected separately, and diluted to 100 c.c. with the turpentine fraction mentioned; a preliminary test will show whether further dilution is necessary to reduce the cineole content to 50%. Ten c.c. of the solution are then shaken, in a flask having a graduated neck, with a warm 55% resorcinol solution for five minutes, a further quantity of the resorcinol solution is then added so as to bring the oil into the neck of the flask, and, after cooling, the volume of the oil is read. W. P. S.

Estimation of Camphor and of Certain Essential Oils when in Solution in Alcohol. W. B. D. PENNIMAN and W. W. RANDALL (*J. Ind. Eng. Chem.*, 1914, **6**, 926—928).—The method proposed depends on the fact that camphor and the essential oils of peppermint, lemon, orange, anise, and nutmeg are liberated from their alcoholic solution when this is mixed with from four to ten times its volume of concentrated calcium chloride solution, and that the separated camphor or oil is soluble in light petroleum, b. p. 40—60°. Within certain wide limits, the increase in volume of the light petroleum is equal to the volume of the camphor or essential oil. A measured quantity of the alcoholic solution under examination is mixed in a flask, provided with a graduated neck, with calcium chloride solution, a definite volume of light petroleum is added (about equal to the volume of the oil to be dissolved), more of the calcium chloride solution is added to bring the mixture into the neck of the flask, the whole is submitted to centrifugal action, and the increase in volume of the light petroleum noted. W. P. S.

Detection of Emodin-bearing Drugs in the Presence of Phenolphthalein. L. E. WARREN (*Amer. J. Pharm.*, 1914, **86**, 444—449).—The red coloration obtained when emodin is treated with an alkali cannot be used for the detection of this substance in mixtures also containing phenolphthalein, but if the latter is converted into tetraiodophenolphthalein, the emodin may be extracted with chloroform and identified by the alkali test. The substance is extracted with acetone or chloroform, the extract is evaporated, the residue dissolved in dilute sodium hydroxide solution, and a slight excess of iodine solution is added. The mixture is then rendered acid with hydrochloric acid, the insoluble tetraiodophenolphthalein is separated by filtration, and the filtrate, after the addition of sodium sulphite, is shaken with chloroform; this chloroform extract is evaporated, and the residue tested with alkali hydroxide solution. In the case of preparations containing phenolphthalein, a faint red coloration may sometimes be obtained, but this disappears on the addition of an excess of the alkali, whilst the coloration given by emodin is permanent. The emodin coloration is of various shades of red according to the source of the emodin. Except in the case of aloes, the method is trustworthy. A method described recently by Bailey (A., 1914, ii, 501) was also found to yield trustworthy results. W. P. S.

Estimation of Prussian-blue in Tea. G. W. KNIGHT (*J. Ind. Eng. Chem.*, 1914, **6**, 909—910).—**The following method is recommended** for the estimation of very small amounts (say, 1 part per 200,000) of added Prussian-blue in tea. One hundred grams of the powdered sample are moistened with 85% phosphoric acid, and distilled until phosphoric acid begins to pass over, the distillate being collected in a receiver containing dilute sodium hydroxide solution. The distillate, if acid, is neutralised, 3 c.c. of 10% sodium hydroxide are added in excess, then a small crystal of ferrous sulphate and a few drops of ferric chloride solution, and the mixture is boiled for one minute. The solution is then acidified with hydrochloric acid, the precipitate collected, washed with alcohol, and dissolved in a small quantity of sodium hydroxide solution. After this solution has been acidified with acetic acid, a few drops of hydrochloric acid and ferric chloride solution are added, followed by more hydrochloric acid, if necessary. The whole is then evaporated to about one-half its bulk, the precipitated Prussian-blue is collected on a filter, washed with dilute hydrochloric acid, water, alcohol and ether, dried at 100°, and weighed. W. P. S.

Reactions of Alanine and Glycine. L. CHELLE (*Ann. Chim. anal.*, 1914, **19**, 67—68; from *Bull. Soc. pharm. Bordeaux*, 1913).—*Alanine.*—About 10 mg. of the substance are dissolved in water, 1 c.c. of glacial acetic acid and 0·5 c.c. of 5% sodium nitrite solution are added, and the mixture is boiled until nitrous vapours cease to appear; 0·1 gram of hydrazine sulphate is then added, the solution is again boiled, and 4 c.c. of concentrated sulphuric acid are added gradually. The resulting solution is divided into three

portions; the addition of a drop of an alcoholic guaiacol solution to one portion produces a red coloration; a yellow coloration is obtained on treating another portion with a drop of an alcoholic codeine solution, whilst the third portion yields an orange coloration on the addition of a drop of *p*-cresol solution. *Glycine.*—The sulphuric acid solution of the diazotised substance yields a reddish-violet coloration with guaiacol, a violet coloration with codeine, and a green coloration with *p*-cresol. The reactions may be obtained with 1 mg. of glycine. W. P. S.

Estimation of Morphine. Lloyd's Reagent. H. M. GORDIN and J. KAPLAN (*Amer. J. Pharm.*, 1914, **86**, 461—464).—When morphine is extracted from a saturated potassium carbonate solution by shaking with a mixture consisting of equal volumes of alcohol and chloroform, the weight of alkaloid found is always too high (from 2 to 15%); this method of extracting the alkaloid is, therefore, untrustworthy. Morphine is precipitated completely by Lloyd's reagent, but only about 90% of the alkaloid can be recovered from the precipitate by shaking this with ammonia and methyl alcohol. It is also impossible to recover the whole of the alkaloid from the precipitate formed when strychnine salts are treated with Lloyd's reagent; this strychnine precipitate is tasteless, but behaves physiologically like strychnine diluted with an inactive substance; the decomposition of the precipitate cannot, however, be brought about by digesting it, in vitro, with pepsin, ptyalin, or trypsin. W. P. S.

Toxicological Investigation of Ergot. F. MARINO-ZUCO and C. DUCCINI (*Gazzetta*, 1914, **44**, ii, 437—447).—The toxicology of ergot has been the subject of but few investigations, which have led to contradictory results. The authors have elaborated the following method for the detection of ergot in viscera, and find that it gives trustworthy indications. The alcohol in which the viscera are usually consigned is separated by filtration, rendered distinctly acid with tartaric acid, and evaporated on a water-bath until the bulk of the alcohol is eliminated. The finely divided viscera and the sediment on the filter are heated for six hours at 75° with double their volume of 95—96% alcohol, acidified with tartaric acid, in a reflux apparatus; the cold alcoholic extract is filtered through new cloth, and the residue firmly pressed. This extraction is repeated with fresh quantities of alcohol until the latter ceases to become coloured, the combined extracts being then evaporated on a water-bath to a small volume. The liquid is mixed with the residue from the alcohol originally present, and the remaining alcohol removed by distillation at a low temperature in a vacuum. The reddish-brown, turbid syrup thus obtained is dissolved in water, and the solution subjected to prolonged shaking with the twofold volume of ether in a large separating funnel; this operation is repeated with fresh quantities of ether so long as the latter becomes coloured. The ether dissolves the red colouring matter and small amounts of fat, whilst the tartrates of any alkaloids present remain in the aqueous solution. The united

ethereal extracts are reduced to a small volume on a water-bath at as low a temperature as possible, and the residual liquid, filtered if necessary, vigorously shaken in an extractor with a small quantity of cold, saturated sodium hydrogen carbonate solution. After a long time, the alkaline layer separates, and exhibits a yellowish-red colour with a faint violet tint or a distinct violet-red colour, if the viscera contained a small or large proportion of ergot. Since this colour reaction may be masked by extraneous colouring matters, the extraction with the alkali is repeated several times, and the total extract carefully acidified with concentrated hydrochloric acid and extracted with ether. The ethereal liquids, which will have a more or less intense orange-yellow colour, are evaporated to a small volume, and the residual liquid is examined spectroscopically; in presence of the red colouring matter of ergot, three absorption bands, with $\lambda = 538$, 499, and 467 respectively, are observed. Prior to the spectroscopic examination, it is well to repeat the extraction with sodium hydrogen carbonate, acidification, and extraction with ether at least five or six times, in order to obtain a sufficiently pure ethereal solution of the colouring matter.

The aqueous tartaric acid liquid remaining after the extraction with ether is rendered distinctly alkaline by means of saturated sodium carbonate solution, and the liberated alkaloids dissolved by shaking several times with ether. The faintly yellow ethereal solution is concentrated to a small volume at as low a temperature as possible, the residue being washed with a little water, in which ergotinine is insoluble. The ergotinine is then either purified by Tanret's method (A., 1878, 679) or converted into its citrate by shaking the ethereal liquid several times with aqueous citric acid; the aqueous solution of the citrate is rendered distinctly alkaline by addition of sodium carbonate, and the ergotinine extracted with ether. Keller's reaction for ergotinine is next applied in the following manner. The residue left on gentle evaporation of the ether is heated slightly on a water-bath with 2—3 c.c. of a 0·1% solution of ferric chloride in glacial acetic acid. The cold liquid, filtered if necessary, is placed in a test-tube, and 2—3 c.c. of concentrated sulphuric acid slowly introduced. If ergotinine is present, a blue ring appears at the surface of separation of the two liquids, and the upper layer assumes a violet colour. If Keller's reaction gives negative results, the ethereal liquid which was extracted with aqueous citric acid should be evaporated, and the residue subjected to the same test.

The above method has always been found to give certain results, provided that the amount of ergot present is not less than 1 gram and that the examination of the viscera is carried out not later than seven days after the interment of the body. Advanced putrefaction of the viscera alters the colouring matter so profoundly as to prevent its recognition. T. H. P.

General and Physical Chemistry.

The Ideal Refractivities of Gases. WILLIAM JACOB JONES and JAMES RIDDICK PARTINGTON (*Phil. Mag.*, 1915, [vi], **29**, 28—35).—A full account of work of which an abstract has already appeared (P., 1914, **30**, 201). H. M. D.

The Magnetic Field of an Atom in Relation to Theories of Spectral Series. H. STANLEY ALLEN (*Phil. Mag.*, 1915, [vi], **29**, 40—49).—On the assumption that the atom may be regarded as a central core carrying an electric charge and producing a magnetic field similar to that due to an elementary magnet, the core being surrounded by electrons in orbital motion, it is shown that a formula for the distribution of lines in spectral series may be derived which is of the same type as the Ritz formula. The energy of radiation, as in Bohr's theory, is supposed to be given out in quanta which represent the differences between the energies in two steady states of motion.

From a consideration of the numerical values of the constants in the derived formula, it is found, however, that the magnetic forces set up by the atom are insufficient to account for more than a small fraction of the effect that would be necessary to give the observed distribution of lines in spectral series. H. M. D.

The Series Spectrum of Hydrogen and the Structure of the Atom. H. STANLEY ALLEN (*Phil. Mag.*, 1915, [vi], **29**, 140—143. Compare Curtis, A., 1914, ii, 761).—According to the measurements of Curtis, the series lines of hydrogen cannot be exactly represented by Balmer's formula. An attempt has been made to ascertain whether the inclusion of the effect of a magnetic field (compare preceding abstract) would lead to results in agreement with observation. The result of this inquiry shows that it is possible to account for the series spectrum of hydrogen on the lines of Bohr's theory if it is assumed that the core of the atom can produce a magnetic field equivalent to that set up by either five or six magnetons. In support of the number 5 is the fact that the magnetic moment produced by an electron moving in a circular orbit with angular momentum $h/2\pi$ is exactly 5 magnetons. On the other hand, the hypothesis of a core of 6 magnetons appears to be supported by the diamagnetic properties of hydrogen. H. M. D.

Spectroscopic Investigations in Connexion with the Active Modification of Nitrogen. IV. A Band Spectrum of Boron Nitride. WILFRED JEVONS (*Proc. Roy. Soc.*, 1915, [*A*], **91**, 120—134. Compare A., 1913, ii, 813).—When the vapour of boron trichloride is introduced into active nitrogen, a very pale bluish-green glow is obtained, the colour of this being very readily distinguishable from the vivid green of the boron flame. The investigation of the spec-

trum of the glow has shown that it consists of the three boron lines λ 3451·50, λ 2497·83, and λ 2496·89, and of a new system of bands with well-defined heads degraded towards the red end, which extend from λ 6371 to at least λ 2140. The same band spectrum is obtained when methyl borate is allowed to come in contact with active nitrogen.

Analysis of the spectrum indicates that it contains two distinct systems, in the less refrangible of which each band consists of four heads, forming two close doublets, whilst the more refrangible system is characterised by single-headed bands, and thus resembles the band spectrum of silicon nitride, described in a previous paper. These bands are not observed in a vacuum tube containing the vapour of boron trichloride, and evidence has been obtained that the band spectrum is due to boron nitride. Boron, carbon, and silicon compounds behave similarly, therefore, in that all give rise to nitride spectra in the nitrogen after-glow.

The boron nitride bands, like the cyanogen bands, are produced in the arc spectrum, where they occur together with the headless, wavy bands of the oxide.

Measurements of the wave-lengths of the heads of the bands are recorded, and formulæ have been deduced to represent them.

H. M. D.

The Spectrum of Palladium. Emil Paulson (*Phil. Mag.*, 1915, [vi], **29**, 154—157).—A discussion of the relations exhibited by the wave-numbers of lines in the palladium spectrum. It is shown that a large number of lines fall into four vertical groups, the corresponding members of which exhibit constant differences in the wave-length numbers. Denoting the four groups by A, B, C, and D, the wave-numbers of these lines are represented by the relations $B=A+1628{\cdot}33$, $C=A+3968{\cdot}00$, $D=A+5159{\cdot}14$. H. M. D.

The Absorption Spectra of Organic Substances in the Light of the Electron Theory. N. P. K. J. O'N. McCleland (*Phil. Mag.*, 1915, [vi], **29**, 192—206).—A theory of absorption is put forward which is based on certain views relative to the constitution of the atom, and it is claimed that this theory makes it possible to predict with reasonable accuracy the positions of the absorption bands of organic compounds from the constitution, when certain fundamental constants are given. In the model of the atom from which these results are obtained, it is supposed that the valency electrons move in circular orbits round a central nucleus. The radius of the orbits is influenced by the mode of combination of the atoms in the molecule, and when light is allowed to act on the system, the electrons are caused to vibrate in their appropriate orbits. Since an electron moving in an orbit represents an electric current, the vibrations of one will affect those of another in accordance with the laws of electrodynamics, and the problem of ascertaining the position of an absorption band is therefore reduced to compounding such vibrations by the mutual induction method.

The method is applied to a number of different systems containing, respectively, one, two, three, and four vibration centres, and

also to the benzene system, in which there are six identical vibration centres arranged in a ring. Other atomic systems corresponding with more complex aromatic compounds are also briefly considered. In this way, a number of constants have been derived, with the aid of which it has been possible to locate the position of the absorption bands in a considerable variety of organic compounds. Except in the case of very complex substances, the difference between the observed and calculated positions is as close as can be expected. H. M. D.

Quantitative Measurements of the Absorption of Light. I. The Molecular Extinctions of the Saturated Aliphatic Ketones. FRANCIS OWEN RICE (*Proc. Roy. Soc.*, 1914, [*A*], **91**, 76—92. Compare Stewart and Baly, T., 1906, **89**, 489).—The ultra-violet absorption of fourteen saturated aliphatic ketones has been investigated. In most cases the ketones were purified by conversion into the bisulphite compounds, in others by transformation into the semicarbazones.

The experimental data show that the wave-lengths of the centres of the absorption bands depend on the number of methyl groups in the α- and β-positions relative to the carbonyl group. Substitution of hydrogen atoms in the γ or further positions has no influence on the position of the band. For ketones of the general formula $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2R$, in which R is a saturated alkyl radicle, the position of the centre of the band is at λ 2790, and for those represented by the formula $RCH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2R$ the centre is at λ 2820.

The substitution of an α-hydrogen atom by methyl causes the centre of absorption to shift towards the red, and from the data for acetone, methyl ethyl ketone, methyl *iso*propyl ketone, and pinacolin it is found that the shifts corresponding with the successive substitution of the three α-hydrogen atoms are 23, 50, and 30 Ångström units respectively. The author considers that these measurements show the existence of a relationship between the optical and the chemical properties. The general results exhibit a certain parallelism with the observations on the magnetic rotation of the ketones, for whereas the magnetic rotatory power is normal in the case of methyl *iso*propyl ketone and the higher homologues, it is abnormal for methyl ethyl ketone, and still more abnormal for acetone.

Spectrophotometric measurements of the extinction-coefficient (ϵ) have also been made, and these data show that the molecular extinction $M=\epsilon/c$, where c is the molar concentration of the ketone, has the same value (21·2) for all the ketones examined, with the exception of acetone and methyl ethyl ketone. Moreover, the molecular extinction curves are absolutely identical for ketones of the general formula $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2R$, whilst for the remainder, excepting acetone and methyl ethyl ketone, the curves are geometrically similar.

On the assumption that the smaller absorption power of acetone is due to association, the author obtains 1·24 for the association

factor. This is in close agreement with the value 1·26 derived from the temperature-coefficient of the molecular surface energy. In a similar way, the association factor of methyl ethyl ketone is found to be 1·09.

The observations are said to be in agreement with the theory that the ultra-violet absorption is due to the electromagnetic field of the carbonyl group as influenced by the substituents in the immediate neighbourhood. H. M. D.

Coloration of Some Derivatives of Picrylmethylamine with Alkalis. A. P. N. Franchimont and H. J. Backer (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 647—653).—In continuation of an investigation of the colour of picrylalkylnitroamines (A., 1914, ii, 84), the authors have investigated the absorption of alcoholic solutions of a number of derivatives of picrylmethylamine of the general formula $C_6H_2(NO_2)_3$·NMe·X, in which X represents one of the groups NO, COMe, CO_2Me, CO_2Et, C_6H_5. As was found in the case of the nitro-group, the nitroso- and the acyl-groups greatly diminish the colour of picrylmethylamine, and, according to the absorption curves, the absorption bands at $1/\lambda = 2390$ and 2875 completely disappear. The same effect is observed if picrylmethylamine is dissolved in concentrated sulphuric acid.

On addition of alkali, the absorption curves for the acyl derivatives show well-marked bands with their heads at about $1/\lambda = 2000$ and 2350, which are therefore practically identical with the bands exhibited by picrylmethylnitroamine. Phenylpicrylmethylamine in the absence of alkali shows an absorption in this region, but the addition of alkali intensifies the absorption, and the curve for the alkaline solution shows maxima at $1/\lambda = 2070$ and 2400.

The absorption curve for picrylmethylnitrosoamine in alkaline solution indicates that it is rapidly decomposed, with the formation of the picrate of the alkali metal. The same change occurs with the acyl derivatives, but much more slowly.

The authors consider that the absorption bands are due to the interaction of the base with one or more of the nitro-groups of the benzene nucleus. H. M. D.

Confirmation of the Law of Bunsen and Roscoe for the Photochemical Reaction of Hydriodic Acid. E. Jimeno Gil (*Anal. Fis. Quim.*, 1914, **12**, 534—539).—A study of the photochemical oxidation of hydriodic acid. The results are in agreement with the law of Bunsen and Roscoe, $it = \text{const.}$, in which i represents the intensity of the illumination and t its duration. Both an electric arc and a mercury vapour lamp were employed as the source of light. A. J. W.

Organic Syntheses by means of Sunlight. XI. General Considerations. E. Paternò (*Gazzetta*, 1914, **44**, ii, 463—475).—The author sums up, in general terms, the results of his investigations on this subject during the past six years. The principal types of reaction observed to occur under the influence of sunlight are as follows:

(1) Carbonylic compounds, such as aldehydes and ketones, react on olefinic hydrocarbons, with rupture of the double linking of the latter and formation of the closed-chain trimethylene oxide and its derivatives. This so-called trimethylenic condensation takes place generally, but not universally, and does not occur with oxygenated compounds other than aldehydes or ketones.

(2) Ketones react with aromatic hydrocarbons and other aromatic compounds, thus: $2C_{13}H_{10}O + 2C_6H_5Et \longrightarrow C_{26}H_{22}O_2 +$ CHPhMe·CHPhMe, the ketone undergoing reduction to pinacone. This doubling of the carbon atom chain takes place also with such compounds as β-phenylpropionic acid, which forms βγ-diphenyladipic or αβ-dibenzylsuccinic acid. In no instance has the author been able to prove the union of two aromatic nuclei in this way (see A., 1914, ii, 321; Ciamician and Silber, A., 1912, i, 537).

(3) Between ketones and aromatic hydrocarbons and other aromatic compounds, a second reaction occurs at the same time as, and perhaps more generally than, the preceding one. In this, direct addition takes place, with formation of a tertiary alcohol, benzophenone and phenylacetic acid, for example, yielding αββ-triphenyl-lactic acid. This change, termed enolic condensation, takes place principally between the carbon of the ketonic carbonyl and the methylene group, the aromatic nuclei playing no part. Enolic condensation is observed also between bases and ketones, benzophenone giving with benzylamine the compound $OH·CPh_2·CHPh·NH_2$, with nicotine a new alkaloid,

$$C_{10}H_{13}N_2·CPh_2·OH,$$

and with *p*-toluonitrile the compound $OH·CPh_2·CH_2·C_6H_4·CN$.

(4) Further, ketones react with hydrocarbons, more especially with the paraffins, and with some of their derivatives in a manner which has not yet been clearly characterised (compare A., 1909, i, 240), but probably consists in the conversion of two mols. of the ketone into pinacone, and the union of a third molecule of ketone with one of the paraffin to form an oxytrimethylene compound, $3C_{13}H_{10}O + C_nH_{2n+2} = C_{26}H_{22}O_2 + C_{13}H_{10}O{\cdot}C_nH_{2n}$. This reaction is given also by cyclic hydrocarbons, and by ethers, acetals, and similar compounds.

The formation of numerous synthetic resins, the preparation of colloidal substances from sparteine and from strychnine, the transformation of pyrone into a carbohydrate similar to the pentosans, the formation of nitrogenous organic compounds by the reduction of nitrates, the synthesis of *photo*-acetophenone and its analogues, and the possibility of introducing complex side-chains into the molecules of the vegetable alkaloids, with formation of derivatives of pharmacological applicability, are all important points resulting from the author's investigations. T. H. P.

Reduction of Aromatic Ketones. III. Photochemical Phenomena. J. Böeseken and W. D. Cohen (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 849—870. Compare A., 1913, i, 1062).—The reduction of an aromatic ketone in a perfectly neutral

medium does not proceed any further than to the pinacone. A series of ketones dissolved in a great variety of anhydrous alcohols and a few other substances have been exposed to sunlight or to the light of a mercury lamp; in all cases where reduction occurs, not a trace of the hydrol is formed, the ketones being quantitatively changed to the pinacones. The addition of sodium ethoxide to the alcoholic solution results in the formation of the hydrols, as is to be expected (*loc. cit.*). The authors deduce, therefore, that in the reduction of aromatic ketones the hydrogen unites exclusively with the oxygen; the resulting half-pinacone polymerises to the pinacone, and the latter, in the presence of hydroxyl ions, is transformed into an equal molecular mixture of the ketone and the hydrol.

Water acts as a powerful negative catalyst; in 80% alcohol, reduction of benzophenone does not occur after exposure for months, whereas in absolute alcohol, under the same conditions, 40% of benzopinacone is obtained after ten hours.

The reduction of benzophenone has been investigated in methyl, ethyl, propyl, *iso*propyl, *iso*butyl, *n*-heptyl, *sec.*-octyl, hexadecyl, allyl, benzyl, and cinnamyl alcohols, in geraniol, *cyclo*hexanol, benzhydrol, and in β-methylbutan-β-ol, γ-methylpentan-γ-ol, and δ-methylheptan-δ-ol. Reduction does not occur in hexadecyl or cinnamyl alcohol, proceeds very slowly in the last three alcohols and in geraniol; and takes place rapidly and quantitatively in the saturated alcohols; the reaction in methyl alcohol, however (and also in allyl alcohol), is much slower than in the other primary and secondary alcohols. Under the influence of light, toluene or *cyclo*hexane reduces benzophenone, whilst hydrogen itself does not.

By employing a constant source of light and allowing this to act on the different solutions under the same conditions, relatively quantitative results are obtained. The experiments lead to the following generalisations. The velocity of pinacone-formation appears to be independent of the concentration of the benzophenone and proportional to that of the alcohol. The temperature-coefficient is small, 1·06—1·11 per 10°. The velocity is greatly dependent on the ketone; benzophenone is attacked rapidly, most of the other aromatic ketones as yet examined are reduced less rapidly, and many of them are not reduced at all. The ratio of the velocities of pinacone-formation in different alcohols is constant. The ratio of the velocities of pinacone-formation in sunlight and in the light of the mercury lamp is the same. When two ketones are present in one solution, one of them absorbs a part of the rays required by the other; the same is true when the light passes through a solution of the one ketone and falls on that of the other.

The light which is active in the reduction of aromatic ketones is situated in the spectrum between 400 μμ and 430 μμ, and very probably in, or adjacent to, the rays 404·7 μμ and 407·8 μμ of the mercury lamp. C. S.

Acquired Radioactivity. Sir William Crookes (*Phil. Trans.*, 1914, [*A*], **214**, 433—445).—Experiments, extending over several years, are described on the action of radium and its emanation on various substances, with especial reference to the diamond. Bombardment of a large number of crystals and phosphorescent substances by cathode rays in a vacuum confers no radioactivity on them, and the substance, both to electrical and photographic tests, remains inactive. The phosphorescence of the diamond under the action of radium is due to the β- and γ-rays, but these produce no coloration. Placing a diamond in contact with a radium compound for long periods produces a coloration, usually bluish-green, which is an effect of the α-rays. Diamonds so treated acquire an enduring activity, in which no apparent diminution occurs after ten years, and neither the colour nor the radioactivity is removed by long treatment with a hot mixture of potassium chlorate and nitric acid. After being cut, the diamond became quite colourless and free from radioactivity.

The activity so acquired consists of α-, β-, and γ-rays. Experiments with glass, quartz, and other materials, buried in radium preparations for long periods and deeply coloured by the action of the rays, showed that the diamond behaves differently from other substances, and alone retains its acquired radioactivity after chemical treatment. Lead glass so treated became almost inactive after boiling in dilute nitric acid, but diamond retained the greater part of its activity after boiling with fuming nitric acid mixed with potassium chlorate. A difference also appeared in the distribution of the radiations from the surface. A quartz crystal rendered radioactive, and laid on a photographic plate, gave an image of the geometric pattern, arising from the superficial activity, of the kind studied by Rutherford, but the image from a radioactive diamond suggested rather a brush discharge from the corners of the crystal. F. S.

Application of the Theory of Allotropy to Electromotive Equilibria. III. A. Smits and A. H. W. Aten (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 680—694. Compare A., 1914, ii, 165, 420, 611).—The theory of allotropy, described in previous papers, is applied in explanation of the phenomena of electrolytic polarisation and of the passive condition of metals. Experiments are described which are said to support the view that the seat of the polarisation effects and of the passivity is not in the boundary layer separating the metal and the electrolyte solution, but in the surface of the metal itself. For the most part, the observations consisted in measuring the changes in the *E.M.F.* of cells of the type:—metal | salt solution | calomel electrode, after the metal had been subjected to the action of acids, of anodic or cathodic polarisation, or of bromine water. The metals used were cobalt, nickel, iron, and chromium, which, according to previous experiments, are characterised by the slow rate at which the internal equilibrium is re-established when this equilibrium in the surface layer of the metal has been disturbed by electrolytic or chemical action.

Under the influence of the above-mentioned agencies, the four metals investigated become distinctly less electropositive, as would be expected according to the theory put forward by Smits.

Of particular interest are some of the observations made with iron. After anodic polarisation, and after etching with strong nitric acid, the potential difference between iron and 0·1*N*-ferrous sulphate solution decreases fairly rapidly, then remains constant for a time before beginning to fall again. The temporarily constant potential difference has the same value whether the passivity of the metal is brought about by anodic polarisation or by the action of strong nitric acid.

It is claimed that none of the older views on passivity affords such a satisfactory explanation of the observed facts as that which is based on the theory of allotropy. In certain respects, Finkelstein's theory offers a certain resemblance to the theory put forward by the authors, but there is a fundamental difference between the two. Whereas Le Blanc's theory considers that passivity is determined by retardation of the process of ionic hydration, the new theory attributes the effect to retardation of changes occurring in the surface layer of the metal. H. M. D.

Allotropy of Cadmium. IV. Ernst Cohen and W. D. Helderman (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 638—641. Compare A., 1914, ii, 652).—As a result of the examination of a large number of cells arranged according to the scheme, electrolytic cadmium | cadmium sulphate solution | 12·5% cadmium amalgam, it has been found that some show an *E.M.F.* at 25° of 0·050 volt, others 0·048 volt, and others, again, 0·047 volt. The *E.M.F.* of cells of the first group decreases spontaneously to 0·048 volt, at which value the *E.M.F.* remains constant.

In the expectation that cells giving 0·048 volt would be found to contain β-cadmium and those giving 0·047 volt α-cadmium, two such cells were examined at 25° and 64·5°. The two cells were connected up so as to have an amalgam electrode in common, and readings were taken until the *E.M.F.* became constant. The final readings show that the cell with the lower *E.M.F.* at 25° has the higher *E.M.F.* at 64·5°. From this observation, the authors draw the conclusion that the *E.M.F.* of 0·048 volt corresponds with β-cadmium; it is also probable that the cell giving 0·047 volt contains α-cadmium, and that giving 0·050 volt, γ-cadmium.

H. M. D.

Electro-deposition of Lead. F. C. Mathers and B. W. Cockrum (*Met. and Chem. Eng.*, 1914, **12**, 714—715; from *J. Soc. Chem. Ind.*, 1914, **33**, 1158—1159).—A smooth, finely crystalline deposit of lead is obtained as follows. Twelve and a-half grams of aloes are shaken with 500 c.c. of warm water, and the insoluble gum or tar is dissolved in 25—50 c.c. of glacial acetic acid. The acid solution is added to the bath, which contains 100 grams of lead acetate and 40 grams of ammonium perchlorate per litre. A

current density of 3·6 amperes per sq. ft. for thick deposits and 7·2 amperes per sq. ft. for thin deposits may be used.

With lead lactate or formate solutions, the baths should contain 4% of lead as lactate or 2% as formate, 1—5% of lactic or formic acid, 4% of ammonium perchlorate, and 0·25% of Barbadoes aloes, the mixture being warmed and filtered before use. A current density of 3·6 amperes per sq. ft. may be used. Sodium naphthalenesulphonate may be used instead of ammonium perchlorate.

C. S.

Hermann's Phenomenon. George Stanley Walpole (*Proc. Roy. Soc.*, 1915, [*A*], **91**, 134—147).—It has been shown by Hermann, that when a current is passed from a dilute solution of a salt to one more concentrated, acid is liberated at the boundary layer, and that alkali is set free at the same place when the current is passed in the opposite direction. These observations have been confirmed and extended by the author.

The experiments were made with a special form of transport apparatus, designed to facilitate the formation and investigation of the boundary layers. The results obtained show that the quantities of acid and alkali liberated bear no relation to the quantity of electricity passed through the circuit. For all the neutral salts examined, the acid is always liberated when the current passes from the more dilute to the more concentrated solution, and the alkali when the current passes from the concentrated to the more dilute. Other conditions being the same, the same quantity of acid and alkali is liberated whatever neutral salt is present in the solutions.

The explanation suggested for this phenomenon is based on the difference in the velocity of the hydrogen and hydroxyl ions on opposite sides of the boundary layer. This difference is determined by the fall of potential per unit length, which depends essentially on the conductivity of the two solutions. The quantities of acid and alkali set free can be calculated from the potential gradients in the two solutions, the time for which the difference of potential is maintained, the resistance constant of the apparatus, the dissociation constant of water, and the mobilities of the hydrogen and hydroxyl ions. Actual experiments afford numbers which are in approximate agreement with the calculated quantities.

H. M. D.

Luminous Vapours Distilled from the Arc, with Applications to the Study of Spectrum Series and their Origin. II. Hon. R. J. Strutt (*Proc. Roy. Soc.*, 1914, [*A*], **91**, 92—103. Compare A., 1914, ii, 599).—The vapour of mercury, distilling from the arc into a vacuum, exhibits luminosity when the vapour has traversed considerable distances beyond the range of the electric field of the arc. The luminosity may be caused to disappear by application of an independent electric field, and the experiments described by the author were made in order to elucidate the nature of this effect in mercury and certain other metallic vapours.

From experiments in which the conducting properties of the luminous jet were examined by means of an auxiliary electrical circuit, it is found that the conductivity depends essentially on the shape and position of the cathode, and is independent of the position of the anode. The fall of potential is almost completely confined to the immediate neighbourhood of the cathode. These facts indicate that the electrical properties of the glowing vapour are similar to those of a flame, which is characterised by the great mobility of the negative ions compared with the positive.

The luminosity is not affected when the stream of mercury vapour passes the anode, but is more or less completely quenched when it reaches the cathode. Although the removal of negative ions at the anode is incomplete, it is considerable enough to show conclusively that the luminosity is independent of the number of negative ions present. It follows from this that the luminous emission is not due to recombination of ions, and it is supposed that the luminous centres are positively charged ions which are survivors of those which are generated in the arc itself. Since the time required for the vapour to travel down the tube is of the order of 1/1000 of a second, it must be assumed that the ions remain luminous for what must be considered as a very considerable interval of time.

Experiments with the vapours of sodium, potassium, calcium, magnesium, zinc, cadmium, and thallium have also shown that the line spectra are extinguished when the luminous vapour passes through a negatively electrified net. In some cases (sodium, magnesium, zinc) the lines of one series are more easily extinguished than those of another. Thus, the sodium lines of the subordinate series are all influenced to about the same extent, but the *D*-line is much less affected. From this it is inferred that the centres of emission are not the same for the two series of lines.

The luminous jets formed by arsenic and antimony are not quenched by passing through a negatively electrified net. The band spectrum exhibited by these elements is therefore, presumably, due to uncharged centres, whilst the band spectrum of magnesium hydride is apparently emitted by positively charged centres. H. M. D.

Emissivity of Metals and Oxides. II. Measurements with the Micropyrometer. G. K. Burgess and R. G. Waltenburg (*J. Washington Acad. Sci.*, 1914, **4**, 566—567).—It has been found that the micropyrometer described in a previous paper (*ibid.*, 1912, **3**, No. 7) may be employed for the determination of the monochromatic emissivities of substances in very small quantities (of the order of 0·01 gram) with an accuracy of about 1%. The data obtained with red light of wave-length $\lambda=0{\cdot}65\,\mu$ and $\lambda=0{\cdot}55\,\mu$ are recorded for a number of metals and metallic oxides, the emissive powers being compared with that of solid platinum.

The temperature-coefficient of the emissivity is very small for all the metals investigated, and for most, this coefficient is negligible. In the case of the white metals, the emissive power

shows very little or no change at the melting point, but there is a marked discontinuity for gold, silver, copper, and uranium. The behaviour of palladium is anomalous, in that the emissivity proper to the liquid may persist after solidification, thus affording an instance of an undercooling radiation effect. The fact that platinum shows a change in emissive power on melting is of some consequence, since the Violle standard is usually defined in terms of the luminous radiation from platinum at its melting point.

H. M. D.

Experiments with Liquid Helium. Preliminary Determination of the Specific Heat and the Thermal Conductivity of Mercury at Temperatures Obtainable with Liquid Helium, and Measurements of Thermo-electric Forces and Resistances for the Purpose of these Investigations. H. KAMERLINGH ONNES and G. HOLST (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 760—767. Compare A., 1914, ii, 832).—As a result of the investigation of a number of thermo-electric couples, it is found that these are unsuitable for the measurement of temperature at liquid helium temperatures. In accordance with theoretical anticipations, the thermo-electric power of all the couples investigated, approaches zero at helium temperatures. On the other hand, it is found that satisfactory measurements of temperature may be obtained with resistance thermometers of manganin and constantin.

The apparatus employed in the measurement of the specific heat of mercury was similar to that described by Nernst (A., 1910, ii, 263). The value obtained was 0·00142 for the mean specific heat between 4·26° and 6·48° (abs.), and 0·000534 between 2·93° and 3·97° (abs.). By making use of Debye's formula for the variation of the specific heat, c, with the temperature, T, $c=kT^3$, in which k is a constant, the authors' data are compared with the results obtained by Pollitzer at higher temperatures. It is found in this way that the specific heat at helium temperatures cannot be satisfactorily represented by the formula in question.

The measurements of the thermal conductivity gave $k=0·27$ between 4·5° and 5·1° (abs.), and 0·40 between 3·7° and 3·9° (abs.). No evidence of the discontinuity which is shown by the electrical conductivity of mercury at 4·19° (abs.) was found in the case of the specific heat or of the thermal conductivity. H. M. D.

Heat of Fusion and the Periodic System. JULIO GUZMÁN CARRANCIO (*Anal. Fis. Quim.*, 1914, **12**, 526—534).—The results of experiments on the heat of fusion of the elements indicate that the heat of fusion per gram is a periodic function of the atomic weight, and for analogous elements of the same group of the periodic system decreases with increase of atomic weight. A similar periodicity is displayed by the quotients obtained by dividing the absolute temperatures of fusion by the atomic weights. The atomic heats of fusion do not exhibit a corresponding periodicity. A. J. W.

The Correction of about 1/66 in the Determination of the Freezing Point of Dilute Aqueous Solutions Supercooled by 1°. M. C. DEKHUYZEN (*Chem. Weekblad*, 1915, **12**, 24—28).—The author advances arguments and experimental evidence in support of his contention that a correction of about 1/66 should be deducted from the reading in cryoscopic determinations with aqueous solutions. The correction must be determined for each apparatus independently, and the volume of solution employed should be 15—20 c.c. A. J. W.

Determination of Vapour Tensions at Low Temperatures. E. JIMENO GIL (*Anal. Fis. Quim.*, 1914, **12**, 469—482).—An account of results obtained in the determination of vapour tension at low temperature. The values obtained for each substance at the highest and lowest point of observation on the absolute scale are: ethyl alcohol, 0·00126 (173·1°) and 0·8349 (243·1°); ethyl ether, 0·005156 (160·1°) and 0·6963 (195·1°); toluene, 0·00170 (183·1°) and 0·8937 (246·1°); acetone, 0·00837 (180·1°) and 0·8763 (212·1°); methyl acetate, 0·00354 (138·1°) and 0·6240 (213·1°).

A. J. W.

Variation of the Triple Point of a Substance with Hydrostatic Pressure. ALFRED W. PORTER (*Phil. Mag.*, 1915, [vi], **29**, 143—149).—Since the saturation vapour pressure of any liquid or solid is a function of the hydrostatic pressure, it follows that the triple point will vary with change in the hydrostatic pressure. It is shown that the variation of the triple-point temperature with hydrostatic pressure is equal to the corresponding change of the melting point. Under atmospheric pressure, the triple point is therefore identical with the melting point. H. M. D.

The Surface Tension of Molten Metals. SYDNEY W. SMITH (*J. Inst. Metals*, 1914, **12**, 168—213).—The method used is that of measuring the depression in a capillary tube electric light carbon. The metal is melted in a plumbago crucible in an electric furnace, a reducing atmosphere being maintained. The level is measured by means of an insulated steel wire, which is lowered vertically into the carbon tube by a micrometer depth gauge until an electrical contact is made. The results are sufficiently concordant. The metals examined are mercury, tin, bismuth, lead, zinc, antimony, aluminium, silver, gold, and copper.

The surface tension of molten metals is a periodic function of their atomic weight, metals with the largest atomic volumes having the least surface tensions. The metals which are known to have the greatest effect in lessening the cohesion of gold are those which are nearest to gold in atomic weight, but with much larger atomic volumes, and therefore lower surface tensions, such as lead and bismuth.

The effect of other metals in dilute solution on the surface tension of mercury is also a periodic function of their atomic weight (Schmidt, A., 1913, ii, 190). C. H. D.

Coefficient of Diffusion in Dilute Solutions. BASIL W. CLACK (*Proc. Physical Soc. London*, 1914, **27**, 56—68).—The apparatus described in previous papers (*ibid.*, 1908, **21**, 863; 1911, **24**, 40) has been improved, with the result that accurate measurements of the diffusivity of salts in aqueous solution can now be obtained in a few days. The special feature of the apparatus consists in the suspension of flasks filled with the solution under examination from the arms of a delicate balance in a large volume of water, the temperature of which is kept constant. Each flask is fitted with a battery of narrow tubes, through which the salt diffuses upwards. The diffusion tubes attached to the two flasks are of equal length, but differ considerably in sectional area, and an arrangement is provided whereby the concentration of the solution is kept constant at each end of the tubes. The actual manipulation during the process of diffusion consists in determining the rate of change in weight of the flasks, which in the improved apparatus attains a constant value after a very short time. It is, in fact, possible to obtain fairly accurate values for the coefficient of diffusion in experiments which only last one day.

The results obtained show that at 18° the coefficient of diffusion $K.10^5$) for potassium chloride increases from 1·388 in 0·05N-solution to 1·584 in 2·0N-solution; for potassium nitrate it decreases from 1·453 in 0·05N- to 1·190 in 1·0N-solution; and for sodium chloride it increases from 1·165 in 0·05N- to 1·253 in 2·0N-solution. H. M. D.

A Theory of Supersaturation. W. J. JONES and J. R. PARTINGTON (*Phil. Mag.*, 1915, [vi], **29**, 35—40).—The authors discuss the question of the influence of surface energy on the solubility of solids in liquids, and on the formation and stability of supersaturated solutions. The theoretical argument indicates that the size of "active" particles of solid, that is, such as induce crystallisation in a given solution, decreases with fall or rise of temperature, according to whether the solid dissolves in its nearly saturated solution with absorption or development of heat. The spontaneous crystallisation of supersaturated solutions of the first, more frequently occurring, type, when these are cooled below a certain temperature, is attributed to this reduction in the size of the "active" particle. At a sufficiently low temperature, it may be assumed that the necessary size is only a relatively small multiple of the size of the molecule of the dissolved substance. H. M. D.

The Widmanstätten Structure in Alloys and Metals. N. T. BELAIEW (*J. Inst. Metals*, 1914, **12**, 46—55).—The Widmanstätten structure, which is characteristic of meteorites, is not confined to alloys of iron. It may be produced either by transformations in the solid state or by crystallisation from solid solution. Several examples are given. C. H. D.

The Metastable Continuation of the Mixed Crystal Series of Pseudo-Components in Connexion with the Phenomenon of Allotropy. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 672—678. Compare A., 1914, ii, 546).—A theoretical paper, in

which the author discusses the transition from monotropy to enantiotropy under the influence of pressure. It is also shown that a system which shows no sign of phase allotropy under its own vapour pressure may become monotropic when the pressure is raised, and that enantiotropy may be exhibited at higher pressures in the absence of monotropy under the characteristic vapour pressure of the system. H. M. D.

Gas Equilibria and a Test of van der Waals' Formula. I. F. E. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 695—703).—The formulæ for the equilibrium constants of gaseous systems derived by van der Waals, Sackur, and Tetrode have been examined by reference to the data for the system $I_2 \rightleftarrows 2I$. On the assumption that the iodine molecule is represented by two spheres, the masses of which are concentrated in centres separated by a distance d, these formulæ give limiting values for d equal to $1{\cdot}6 \times 10^{-8}$ and $0{\cdot}7 \times 10^{-9}$ cm. van der Waals' formula, which takes into account the variability of the specific heat with the temperature, yields for the atomic distance $d = 0{\cdot}82 \times 10^{-8}$ cm.

H. M. D.

Unmixing in a Binary System for which the Three-Phase Pressure is Greater than the Sum of the Vapour Tensions of the Two Components. F. E. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 834—839).—It has been shown previously (A., 1914, ii, 40) that the three-phase pressure in the system hexane–water is greater than the sum of the vapour pressures of the pure components when the temperature is not far removed from the critical solution temperature. Further investigation of liquid pairs has shown that the same behaviour is exhibited by "normal pentane" (a mixture of *n*- and *iso*-pentane) and water, and also by benzene and water. The difference for the first pair increases from 0·4 atmosphere at 150° to 1·8 at 187·1°, which is the critical end-point. For the second pair, the difference increases from 0·45 atmosphere at 210° to 2·95 at 267·8° (critical end-point). It is supposed that the relation in question is characteristic of systems for which the critical end-points are lower than the critical temperatures of the two components. Binary systems, for which the critical end-point falls between the critical temperatures of the components, do not exhibit the above relationship, according to the data which are available for examination. For such systems, the three-phase pressure is less than the sum of the vapour pressures of the components. H. M. D.

Equilibria in Ternary Systems. XVII. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 767—781. Compare A., 1914, ii, 807).—A further discussion of the equilibrium relations for the case in which two of the three components are volatile, and in which a solid binary compound is formed by combination of the non-volatile with one of the volatile components. H. M. D.

Equilibria in the System Pb–S–O; the Roasting Reaction Process. W. REINDERS [with F. GOUDRIAAN] (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 703—718).—In order to obtain information in regard to the nature of the changes which occur during the manufacture of metallic lead from galena by the roasting process, the authors have investigated the equilibrium relations in the ternary system with lead, sulphur, and oxygen as components. For the most part, the experiments consisted in the determination of the vapour pressures at temperatures between 500° and 800°, and in the examination of the solid phases present under varying conditions of temperature and pressure.

The collective data indicate that when sulphur dioxide is removed from a mixture of lead sulphide and lead sulphate, the following univariant systems, characterised by the presence of three solid phases, are successively met with: (1) PbS–$PbSO_4$–$PbO,PbSO_4$; (2) Pb–PbS–$PbO,PbSO_4$; (3) Pb–$PbO,PbSO_4$–$2PbO,PbSO_4$; (4) Pb–$2PbO,PbSO_4$–$3PbO,PbSO_4$; (5) Pb–$3PbO,PbSO_4$–PbO. The metallic phase probably contains a little dissolved lead sulphide, the proportion of which varies in the different equilibria. The vapour pressures corresponding with the five systems, and the variation of the pressure with the temperature, are shown in a series of curves.

From the vapour-pressure curve for the first system, the authors find that the thermal value of the reaction $PbS + PbSO_4 = 2Pb + 2SO_2$ is $-99{,}543$ cal. The value calculated from the heats of formation of the compounds involved in this equation is $-92{,}470$ cal. at 20°. H. M. D.

Aspirin. I. Decomposition of Aspirin by Water. D. E. TSAKALOTOS and S. HORSCH (*Bull. Soc. chim.*, 1914, [iv], **15**, 743—747).—A study of the rate of decomposition of aspirin by water alone or in the presence of certain acids. The velocity of the action was measured by determining the increase in acidity, using $N/50$-sodium hydroxide and phenolphthalein as indicator. The decomposition of aspirin by water is very slow at the ordinary temperature, being complete in about 100 days. Acids exert a catalytic influence on the decomposition, which is accelerated by hydrochloric and sulphuric acids. With acetic or citric acid, the action is accelerated up to about the eighth day, after which the velocity of the action is diminished. W. G.

Number Relations Amongst the Elements. F. H. LORING (*Chem. News*, 1915, **111**, 13—15).—A discussion of certain relations exhibited by a periodic arrangement of the elements, which has been described in the author's "Studies in Valency." H. M. D.

Theory of the Metallic State. F. A. LINDEMANN (*Phil. Mag.*, 1915, [vi], **29**, 127—140).—A theoretical paper in which the author discusses the interpretation of the physical properties of metals in terms of the electron theory. It is shown that the free electrons in a metal may not be treated as a gas, for a gas can only be a

good conductor of heat if its heat capacity is large. Experiment shows that the free electrons conduct heat well, but that their heat capacity is too small to be measured. It is suggested that the free electrons form a space-lattice corresponding with a crystal at a very low temperature. The application of this view to the interpretation of the various phenomena which are exhibited by metals is considered in detail. It explains the exceptional behaviour of alloys and, in general outline, the photoelectric effect, but special assumptions are necessary for the derivation of the Wiedemann-Franz law. H. M. D.

Goossen van Vreeswyck, a Mining Engineer and Chemist of 250 Years Ago. W. P. JORISSEN (*Chem. Weekblad*, 1914, **11**, 1075—1086; 1915, **12**, 28—30).—An account of the life and publications of Goossen van Vreeswyck (*ca.* 1630—1690), celebrated for his investigations in the animal, vegetable, and mineral kingdoms in many parts of the globe. A. J. W.

Inorganic Chemistry.

Formation of Ammonia and Hydrogen Cyanide in the Distillation of Coal. OSKAR SIMMERSBACH (*Stahl und Eisen*, 1914, **34**, 1153—1159, 1209—1213).—The coal to be tested is enclosed in a porcelain tube, which is provided with a thermocouple, and is heated in an inclined position in an electric furnace. Before beginning an experiment, the air is displaced by carbon dioxide, previously purified and dried. The upper end of the tube is connected with a manometer containing liquid paraffin, with a gas-sampling vessel, and with the absorption apparatus. The latter consists of two U-tubes containing glass beads and 1 : 1 sulphuric acid, a tube packed with cotton wool, and a long 10-bulb tube containing suspended ferrous hydroxide. Beyond this is the gasometer. At the end of the experiment the carbon dioxide is washed out by means of purified nitrogen.

Tar is recovered by washing out the porcelain tube, sampling vessel, absorbing vessels, and connecting tubes with chloroform, and washing this solution with dilute sulphuric acid to remove ammonia. The acid solutions are united and used for the ammonia estimation. Hydrogen cyanide is estimated in the contents of the ferrous hydroxide tube. A Kjeldahl estimation of nitrogen in the tar and coke is also made. For coke, it is necessary to boil vigorously with concentrated sulphuric acid, then add potassium sulphate, and, after thorough boiling, complete the solution by the cautious addition of small quantities of potassium chlorate.

Various analyses are given, and it is shown, from experiments

with a coal from Upper Silesia, that the percentage of nitrogen in the coke steadily falls with increasing temperature of distillation, whilst that in the gas passes through a minimum at 850°, and then rises rapidly. The percentage of ammonia is a maximum at 850—900°, and only diminishes slightly up to 1200°; 3·5 to 4% of the total nitrogen is found in the tar. The proportion of hydrogen cyanide increases slowly with the temperature. The presence of water vapour increases the proportion of cyanide, and diminishes that of ammonia. C. H. D.

The Vapour-Pressure Lines of the System Phosphorus. A. SMITS and S. C. BOKHORST (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 678—680. Compare A., 1914, ii, 533).—Further investigation of the vapour pressure of red and of violet phosphorus indicates that these cannot be considered as enantiotropic modifications. When equilibrium between solid and vapour is attained, the data yield a continuous vapour pressure-temperature curve, and the authors draw the conclusion that the red and the violet forms of phosphorus differ only in respect of the size of the particles, the violet representing the more coarsely crystalline form.

The behaviour of red or violet phosphorus on volatilisation is considered to afford strong evidence in support of the theory of allotropy put forward by Smits (A., 1910, ii, 195, 400). According to this theory, red or violet phosphorus consists of a mixture of two or more kinds of molecules in equilibrium, and these pseudo-components are supposed to exhibit very considerable differences in volatility. The observed fact that abnormally high vapour pressures are recorded when red or violet phosphorus is rapidly heated to the temperature of the measurement is readily accounted for by the absence of internal equilibrium and the excessive volatilisation of the more volatile pseudo-component. Above 450°, the rate at which the internal equilibrium is reached becomes considerable, and the abnormally high vapour pressures are no longer observed. H. M. D.

A Spongy Modification of Sodium Amalgam. ENRIQUE V. ZAPPI (*Anal. Soc. Quim. Argentina*, 1914, **2**, 210—211).—A specimen of 20% sodium amalgam, contained in an imperfectly closed vessel for more than a year, gradually lost its metallic appearance, and developed a lead-grey colour and foliated structure. Water decomposed it, with formation of mercurous oxide and a spongy substance, similar in appearance to ammonium amalgam.

A. J. W.

Influence of the Gaseous Impurities of Silver on the Values of the Atomic Weights Determined by Classical Methods: Atomic Weights of Chlorine and Phosphorus. PH. A. GUYE and F. E. E. GERMANN (*Compt. rend.*, 1914, **159**, 992—996).—Taking into account the amounts of carbon monoxide and water vapour recently found by them to be present in highly purified silver after fusion in hydrogen (compare A., 1914, ii, 727, 740), the authors

consider that the values obtained by the use of such silver in determinations of the atomic weight of this metal may be 0·0045 too high. They further discuss the effect of such an error on the atomic-weight determination of a number of other elements, based on the use of silver as a standard, and find the necessary corrections to be of the order 0·005 to 0·020, and exceptionally as much as 0·040. Thus for chlorine the atomic weight should be 35·460 instead of 35·455, and for phosphorus 31·007 instead of 31·028.

W. G.

The Hydration of Portland Cement. A. A. KLEIN and A. J. PHILLIPS (*J. Washington Acad. Sci.*, 1914, **4**, 573—576).—In connexion with the investigation of the hydration of Portland cement, experiments have been made on the hydration of mono-calcium aluminate, 5 : 3-calcium aluminate, tricalcium aluminate, mono-calcium silicate, β-orthosilicate, γ-orthosilicate, and tricalcium silicate. Observations were also made with lime burned at different temperatures and ground to various degrees of fineness, and with commercial cements characterised by a high silica, a low silica, a high iron, and a high magnesia content.

The only crystalline product observed in the hydration of the aluminates was hydrated tricalcium aluminate ($3CaO,Al_2O_3,xH_2O$), and this is only formed with a large excess of water. The 5 : 3-aluminate and the mono-calcium aluminate eliminate amorphous hydrated alumina, and form the crystalline hydrated tricalcium aluminate. In contact with a solution of calcium sulphate, the three aluminates also yield a compound of the composition $3CaO,Al_2O_3,3CaSO_4,xH_2O$ ("sulpho-aluminate"). It crystallises in long, prismatic needles.

Monocalcium silicate and the γ-orthosilicate do not undergo hydration, and the β-orthosilicate only takes up small quantities of water after long periods. Tricalcium silicate hydrates readily and quickly yields crystallised hydrated lime and amorphous hydrated orthosilicate.

In the hydration of cement, the first constituent to react is the aluminate, which forms amorphous hydrated tricalcium aluminate, and sometimes amorphous hydrated alumina. The sulpho-aluminate crystals are also formed, and hydration of the low burned or finely ground lime also takes place. These changes occur within a few hours after the gauging of the cement. Within twenty-four hours, the tricalcium silicate begins to hydrate, and this change is generally completed within seven days. Between seven and twenty-eight days, the amorphous aluminate commences to crystallise, and the β-orthosilicate, which is the least reactive compound, also begins to react.

Reference is also made to the influence of these changes on the mechanical properties, and to the action of small quantities of electrolytes on the initial setting of the cement. H. M. D.

The Ternary System $CaO-Al_2O_3-SiO_2$. G. A. RANKIN [with Optical Study by FRED. E. WRIGHT] (*Amer. J. Sci.*, 1915, [iv], **39**, 1—79).—The equilibrium relations exhibited by the binary com-

binations of these three substances have been described in previous papers (A., 1906, ii, 770; 1909, ii, 1015), and a partial account of the ternary system has also been given (A., 1911, ii, 725), in which certain quintuple points and boundary curves were provisionally located. As a result of further experimental work, the equilibrium relations have been more exactly defined, and the present paper gives a detailed record of the results.

The plane projection of the concentration-temperature model shows the existence of fourteen different regions, each of which corresponds with a different solid phase. The characteristic points in this diagram are recorded in a series of tables, which give, respectively: (1) the composition of the compounds, their melting points and transition points; (2) the temperature and composition of the binary eutectics; (3) similar data for quadruple points other than eutectics; (4) the temperature and composition of ternary eutectics; (5) similar data for quintuple points other than eutectics. A further table is given, in which the optical-crystallographical properties of the various unitary, binary, and ternary compounds are recorded.

The temperature-concentration diagram permits of the prediction of the course of crystallisation of any fused ternary mixture. Applied to the case of Portland cement clinker, the results indicate that this is essentially a mixture of the compounds $3CaO,SiO_2$, $2CaO,SiO_2$, and $3CaO,Al_2O_3$, together with some $5CaO,3Al_2O_3$ and possibly a small amount of free lime. This conclusion is in agreement with the results obtained in recent work on commercial Portland cement clinkers. H. M. D.

The Supposed Allotropy of Zinc. CARL BENEDICKS and RAGNAR ARPI (*Zeitsch. anorg. Chem.*, 1914, 88, 237—254).—Several authors have described a transformation point of zinc between 300° and 350°. A further point at about 170° was observed in commercial "zinc puriss." by Benedicks in 1910, but was not confirmed by Werner (A., 1913, ii, 1057).

Kahlbaum's distilled zinc, containing only 0·008% of impurities, has been examined in the cast and also in the drawn condition. The drawn metal, after annealing at 350°, is almost as flexible as lead wire. The electrical resistance-temperature curves are not well suited to showing small irregularities, so that a different graphical method is employed. The abscissæ being t, the ordinates are $W-kt$, where k is a constant. The highly purified zinc gives a smooth curve, without any transformation point. Between 15° and 300°, the resistance is closely represented by the formula $W=5{\cdot}45(1+0{\cdot}0039t+0{\cdot}0000017t^2)$. The addition of 0·5% of cadmium or lead gives rise to breaks in the curve, those for the cadmium alloy being at about 170° and 350° respectively. These points are attributed to the formation of limited solid solutions of cadmium in zinc, the upper temperature being that at which the solidus is intersected, and the lower that at which the curve of solubility in the solid state is crossed. Lead has a similar, but smaller, influence, and is usually present in smaller quantities.

The experiments of Cohen and Helderman (A., 1914, ii, 127) are criticised, on the ground that the zinc used becomes partly converted into a basic salt by contact with the zinc sulphate solution, and that the washing with dilute acid may have caused a loosening of texture, which would account for the diminution of density.

C. H. D.

Allotropy of Zinc. III. Ernst Cohen and W. D. Helderman (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 641—644. Compare A., 1914, ii, 127, 652).—A criticism of the conclusions drawn by Benedicks and Arpi (preceding abstract) from their observations on the influence of temperature on the electrical conductivity of zinc. The change in the physical properties of zinc at higher temperatures cannot be attributed to the presence of impurities. That the change is due to allotropic transformation has been shown by the authors in experiments with pure zinc. H. M. D.

The Allotropy of Lead. I. Ernst Cohen and W. D. Helderman (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 822—828. Compare A., 1914, ii, 652).—Experiments are described which are said to indicate that ordinary lead consists of a metastable mixture of several allotropic modifications of the metal. The lead used in these experiments was very pure, containing only 0·001% of copper and 0·0006% of iron. The metal was melted, chilled in water, and cut into small blocks, which were immersed in a solution prepared from 400 grams of lead acetate, 1000 c.c. of water, and 100 c.c. of nitric acid (D 1·16). After remaining for some days at the ordinary temperature, it was found that the lead shows marked signs of structural change, and after three weeks this becomes so pronounced as to suggest complete disintegration of the metal. The change is illustrated by a series of photographs of the metallic surface.

The transformation is not due to chemical action, but, by means of pyknometric measurements and observations with a dilatometer, it is shown that the change is accompanied by changes in density. These variations in density are not always in the same direction, and obviously depend on the previous history of the metal. The authors draw the conclusion that there are more than two allotropic forms of the metal in the samples under examination.

Closely connected with the above observations is the fact that when pure metallic lead is immersed in the solution mentioned above, or in a concentrated (30%) solution of lead nitrate, a lead tree is formed in a few days, both at the ordinary temperature and at 50°. H. M. D.

Tensile Properties of Copper at High Temperatures. Guy D. Bengough and D. Hanson (*J. Inst. Metals*, 1914, **12**, 56—88. Compare A., 1912, ii, 763).—Tensile tests of copper in a vertical machine, the specimen being heated by gas, show that the properties of the metal are greatly influenced by the composition of the

surrounding atmosphere. The ductility at 800° and upwards is increased considerably by the presence of oxygen. Rolled copper which has not been annealed is stronger, but less ductile, than the same copper which has not been annealed after rolling, at all temperatures up to 1000°, when an atmosphere of carbon dioxide is used. With annealed copper, the fracture passes through the crystals at temperatures below 700°, and between the crystals at temperatures above 750°. At intermediate temperatures, it may take either course. Oxygen or arsenic, alloyed with copper, decreases the strength and increases the ductility at high temperatures. An atmosphere of hydrogen has a weakening effect above 720°, probably owing to reduction of oxide.

The results are best explained by assuming the existence of an amorphous intercrystalline cement, which is stronger than the crystals at low, and weaker at high, temperatures (*loc. cit.*, and also Rosenhain and Ewen, A., 1913, ii, 119; Humfrey, *ibid.*, 778). This cement is probably not identical with Beilby's amorphous material formed by mechanical deformation. C. H. D.

Absorption of Gases by Refined Copper. W. Stahl (*Metall und Erz*, 1914, **11**, 470—482; from *J. Soc. Chem. Ind.*, 1914, **33**, 1158).—The absorption of gases by molten copper increases, in general, with the temperature up to a certain point, with increasing purity of the metal, and with the partial pressure of the gas. The presence of nickel or platinum, however, has a favourable influence on the absorption. Copper, in the solid or liquid state, appears not to absorb water vapour, carbon dioxide, nitrogen, argon, or helium. At 1420°, 61 grams of copper absorb 0·15 c.c. of carbon monoxide; this small quantity markedly affects the physical properties of the refined metal. Hydrocarbons are not occluded by copper, but are decomposed into carbon and hydrogen, the latter being absorbed and the former oxidised. The absorption of hydrogen in, and its diffusion through, copper has been detected even at 650°. Up to 1500°, the absorption of hydrogen increases almost linearly with the temperature, except at the melting point of the metal, where a sudden increase occurs. The solubility per 100 grams of copper is 0·1 mg. at 650° and 1·4 mg. at 1500°; with both solid and liquid copper, the solubility of hydrogen increases as the square root of the pressure. The conductivity of copper is not affected by absorbed hydrogen. By heating copper containing copper oxide in an atmosphere of hydrogen, the gas penetrates the metal and reduces the oxide, and the steam produced escapes by disintegrating the metal.

The dissociation pressure of cuprous oxide is equal to the partial pressure of atmospheric oxygen, 0·21 atmos., at 1662°. When the oxide is in solution in the copper, its dissociation pressure is lowered, so that at 1600° it is certain that thermal dissociation of the dissolved oxide does not occur, and the absorption of oxygen at this temperature is due to chemical combination, not to physical solution.

The preceding results indicate that during the refining of molten

copper, the absorption of carbon monoxide predominates during the end of the "hard poling" period and at the beginning of the "green poling" period, whilst the absorption of hydrogen predominates during the latter period when the oxygen has been removed.

The disintegration of copper which occurs during solidification has been traced to occluded sulphur dioxide, formed by oxidation of the sulphur present; the gas is evolved with "spitting" during solidification, but the cold metal still retains a considerable quantity of the gas. Sulphur dioxide does not diffuse through solid copper below 1000°. The reaction, $Cu_2S + 2Cu_2O = 6Cu + SO_2$, is reversible; the equilibrium of the four substances at all temperatures has been proved in a number of investigations. C. S.

Behaviour of Copper–Zinc Alloys when Heated in a Vacuum. W. E. Thorneycroft and Thomas Turner (*J. Inst. Metals*, 1914, **12**, 214—229. Compare T., 1912, **101**, 585; 1913, **103**, 1534).—When α-alloys of copper and zinc are heated in a vacuum, the rate of volatilisation is nearly proportional to the temperature, but this proportionality is not observed in the alloys richer in zinc. With more than 40% of copper in the alloys, the separation is quantitative, but with alloys containing less copper, a part of the copper volatilises with the zinc. The volatility of zinc is increased by alloying with small quantities of copper. C. H. D.

The Critical Point at 460° in Zinc-Copper Alloys. O. F. Hudson (*J. Inst. Metals*, 1914, **12**, 89—110).—The critical point observed at 460° in brasses containing from 37 to 60% of zinc, and regarded by Carpenter as a eutectoid point (A., 1912, ii, 764; 1913, ii, 138, 139), is considered to be due to a polymorphic transformation of the β-constituent. Structural resolution of β is not observed on annealing at 440°, even in presence of a slight excess of α or γ. Further, when a heterogeneous alloy is prepared by casting a γ-alloy on to copper, so that a zone of β is obtained, bordered above by $\beta + \gamma$ and below by $\alpha + \beta$, the zone of β increases on annealing at 435°, proving that a phase, β', is stable below the transformation point. The β' zone is also formed by diffusion of zinc into solid copper or α-brass at 450°.

It appears that β is more readily supersaturated with α than with γ.

When bronze containing 10% of tin is immersed in molten tin at 300°, diffusion takes place, and a zone of the δ-constituent is formed in immediate contact with the α-bronze without an intermediate zone of $\alpha + \delta$. This condition is also observed in the above experiments with zinc. C. H. D.

[The Influence of Carbon on the Corrosion of Brass.] Arnold Philip (*J. Inst. Metals*, 1914, **12**, 133—167).—In a series of experiments to determine the influence of contact with carbon on the corrosion of brass, sections of condenser tubing, containing 29% zinc and 1% tin, are placed in close contact with broken coke

in a stream of sea-water. A series of similar specimens, in contact with pebbles instead of coke, is used for control. It is found that the corrosion is in all cases greatly accelerated by contact with carbon, owing to local electrolytic action. This conclusion is opposed to that arrived at by Bengough and Jones (A., 1914, ii, 366), and the causes of the difference are discussed at length.

C. H. D.

Binary Copper–Zinc and Ternary Copper–Zinc–Lead Alloys. N. PARRAVANO (*Gazzetta*, 1914, **44**, ii, 475—502).—[With C. MAZZETTI and R. MORETTI.]—The melting-point diagram for copper–zinc alloys differs from those of Shepherd (A., 1904, ii, 662) and of Carpenter and Edwards (A., 1912, ii, 1057) only as regards the equilibrium horizontals at 905°, 838°, 700°, 595°, 545°, and 425°, for which the corresponding durations have been determined. The temperature of the eutectoid transformation, $\delta \longrightarrow \gamma + \epsilon$, which the author finds to be 545°, was given by Shepherd (*loc. cit.*) as 450° and by Tafel (A., 1908, ii, 846) as 550°.

Of the copper–zinc–lead alloys, which exhibit a liquid miscibility gap, seven series were examined, the percentages of lead, constant in the members of any one series, being 2, 4, 10, 15, 20, 30, and 50 respectively. In the first series, the lead remains uniformly distributed throughout the whole mass of the metal. In the series containing 4% Pb, the latter remains moderately evenly distributed with the alloys rich in copper; but as the proportion of copper increases beyond 40%, pronounced liquation begins, and this phenomenon becomes accentuated as the percentage of lead present is augmented. Lead is virtually undissolved in either the α- or the γ-solution, the lead in lead brasses being merely mixed with the crystals of the brass; this conclusion, drawn from the durations of the arrests, is confirmed by the results of Carpenter's investigation of the influence of addition of lead on the critical point at 470° (A., 1913, ii, 139). These results are confirmed by photomicrographs of three of the alloys containing 2% Pb. T. H. P.

The Quaternary System: KCl–$CuCl_2$–$BaCl_2$–H_2O. F. A. H. SCHREINEMAKERS and (Miss) W. C. DE BAAT (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 781—783).—The equilibrium relations in this quaternary system have been described in a previous paper (A., 1913, ii, 53). The solubility data at 40° and 60° are now communicated in detail. H. M. D.

The Basic Sulphates of Copper. H. FONZES-DIACON (*Bull. Soc. chim.*, 1914, [iv], **15**, 723—727. Compare Smith, *Phil. Mag.*, 1843, [iii], **23**, 500).—A study of the conditions governing the formation of the basic sulphates of copper, $CuSO_4,3CuO,4H_2O$ and $CuSO_4,3CuO,5H_2O$, and of the composition of Bordeaux mixture prepared under different conditions. The yield of basic sulphate, for the same strength solutions, is greater when the sodium carbonate is poured into the copper sulphate than in the reverse process. The precipitate, from the same weight of copper sulphate,

is richer in basic sulphate when a very dilute solution of sodium carbonate is poured into a moderately concentrated solution of copper sulphate. On slowly pouring a solution of sodium carbonate into a solution of copper sulphate continuously stirred, if the solution is rich in copper sulphate, the basic sulphate,

$$CuSO_4,3CuO,4H_2O,$$

is formed, but as the concentration diminishes, the basic sulphate, $CuSO_4,4CuO,6H_2O$, is produced. If an excess of sodium carbonate is used, these basic sulphates are converted into the basic carbonate, $CuCO_3,CuO,2H_2O$. If the supernatant liquid is allowed to remain, a precipitate of one of the basic sulphates is formed. W. G.

Supplement to the Phase Diagram of Aluminium-Magnesium Alloys. H. Schirmeister (*Metall und Erz.*, 1914, **11**, 522—523; from *J. Soc. Chem. Ind.*, 1914, **33**, 1159).—The alloys (200 grams in each case) were fused in a nickel wire electric furnace, and the progress of the cooling was registered by a thermo-element and recording galvanometer. The first stationary points were found at temperatures which gradually fell from 657° to 550° as the magnesium increased from 0 to 20%. Second stationary points, denoting a eutectic point, were found at 580—590° with alloys containing 2—15% of magnesium, and a second similar eutectic point was found at 455° with alloys containing 12—15% of magnesium (compare Grube, A., 1905, ii, 523). C. S.

Electrolytic Iron. L. Guillet (*J. Iron Steel Inst.*, 1915, **90**, 66—81).—Electrolytic iron, deposited on a large scale with a revolving cathode and high current densities, using a solution which is neutralised and depolarised by the addition of iron oxide, is hard and brittle, and contains as much as seven volumes of gas, consisting of hydrogen and carbon monoxide. It has a fine structure resembling that of martensite, which becomes less distinct on annealing, but only finally disappears at 800—900°, giving place to the normal structure of pure iron. Annealing below 700° has very little effect on the properties. Using a solution prepared from a pig-iron containing 1% of phosphorus, the iron has been found to contain C 0·004, Si 0·007, S 0·006, and P 0·008%. The position of the critical points is unaffected by the presence of hydrogen, but an additional absorption of heat at 530—690° is observed in the heating curves of the crude iron, which do not recur on cooling. The electrical properties have been examined by Broniewski (A., 1913, ii, 288). C. H. D.

Solubility of Hydrogen and of Nitrogen in Iron. E. Jurisch (*Stahl und Eisen*, 1914, **34**, 252).—The solubility of hydrogen in iron wire containing 0·04% of carbon, determined at atmospheric pressure, increases somewhat more rapidly than the temperature from 416° to 850°. The curve then rises steeply and suddenly until 930° is reached, after which it is approximately parallel to its original direction. The discontinuity is to be attributed to the allotropic change in the iron. The hydrogen is practically all

liberated on slow cooling. Within all three allotropic ranges, the solubility of hydrogen in iron is proportional to the square root of the pressure. Methane is formed between 600° and 930°.

The solubility of nitrogen in reduced iron powder increases very suddenly at 930°, and then slowly falls. The solubility is proportional to the square root of the pressure. C. H. D.

Theory of Hardening and Constitution of Steel. Edward D. Campbell (*J. Iron Steel Inst.*, 1914, **90**, 1—16).—The properties of steel depend largely on the nature of the carbides. It has been shown that the mean molecular weight of the hydrocarbons evolved when annealed steel is treated with an acid decreases as the percentage of carbon increases. Hardened steel gives hydrocarbons of lower molecular weight than annealed steel. It is likely that carbides of lower molecular weight are more soluble in solid iron than those of higher molecular weight, and have a greater hardening effect, and that, with increasing temperature, dissociation of the more complex carbides occurs. Austenite may contain almost completely dissociated carbide. The fact that the hardness of hypereutectoid steel diminishes when the temperature of quenching is raised much above the point at which all the carbide dissolves, corresponds with the theory, as the hardness should be greatest when solution is complete, and dissociation is at a minimum. The facts of specific volume and electrical conductivity are also explained qualitatively. C. H. D.

The Transformations of Steels. H. de Nolly and L. Veyret (*J. Iron Steel Inst.*, 1914, **90**, 165—180).—Dilatometric curves are given for a number of steels in support of the view that iron carbide is partly dissociated in solid solution (compare Campbell, preceding abstract). C. H. D.

The Influence of Coalescence on the Properties of Steel and Alloys. A. Portevin (*J. Iron Steel Inst.*, 1914, **90**, 204—212).—Bronze containing 16% of tin, and consisting of the α- and δ-constituents, is heated in a salt-bath at 525° for an hour, and cooled from 525° to 475° during five hours. After re-heating rapidly to 525°, the slow cooling is repeated. The eutectoid structure disappears, the masses of δ coalescing, and the hardness, measured by Brinell's test, diminishes. The effect on a steel containing 25% of tin is less marked.

Annealing a eutectoid steel at 700° for thirty hours causes coalescence of the pearlite and a great diminution of hardness. A steel containing 0·50% of carbon, annealed at 800° for ten hours and very slowly cooled to 700°, shows segregation of the ferrite into parallel bands without coalescence of the pearlite, whilst annealing for thirty hours at 700° brings about coalescence.

C. H. D.

Behaviour of Slag Occluded in Steel. II. Supposed Solubility of Inclusions of Slag in Liquid Steel. F. Giolitti and G. Tavanti (*Ann. Chim. Applicata*, 1914, **2**, 360—366).—Examina-

tion of the condition and quantity of the reaction slag occluded in a small mass of steel cooled rapidly from the fused state, and of that occluded in the same mass after re-heating, followed by slow or rapid cooling, renders untenable the theory of the solubility of this slag in the steel at a high temperature. A marked difference exists between the behaviour of the reaction slag and that of inclusions consisting largely of sulphides of iron and manganese.

T. H. P.

Molecular Magnitude of Metals in the Solid Phase. M. PADOA and F. BOVINI (*Gazzetta*, 1914, **44**, ii, 528—534).—When a solid solution of concentration C_s separates from a dilute solution of concentration C_1, and the ratio $C_s : C_1$ is constant for solutions of different concentrations, it may be asserted that the solute has the same molecular magnitude in the solid as in the dissolved state. The authors have investigated three different alloys of tin, cadmium, and bismuth. The first two metals form a eutectic and limited solid solutions, which are transformed, at a temperature just above 100°, into the compound, Sn_4Cd; tin and bismuth, and also cadmium and bismuth, give eutectics, but no solid solutions. The ternary alloys examined, which solidify at about 200°, present no further complications. In the three cases, the ratio of the concentration of the cadmium with respect to the tin in the crystals to that in the liquid has the values 0·986, 0·985, and 0·957 respectively. The solid solutions separating from different liquid solutions of cadmium in tin have, therefore, approximately the same concentration, the coefficient of distribution being sensibly constant. The conclusion is drawn that cadmium has the same molecular magnitude in solid solution in tin as in liquid solution, that is, it is monatomic.

These results tend to confirm Stoffel's data concerning these ternary alloys (A., 1907, ii, 357). T. H. P.

The Allotropy of Antimony. ERNST COHEN and J. C. VAN DEN BOSCH (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 645—647).—Evidence has been obtained that so-called metallic antimony is a metastable system which consists of more than two allotropic modifications. From experiments with a dilatometer containing metallic antimony, which had been melted, rapidly cooled, and then powdered, a transition point was found at about 101°. This agrees with the observation that the density of the substance was lowered on heating for four days at 102·5°.

That the equilibrium relations are of a somewhat complicated character is shown by the fact that a dilatometer, which had been heated for fifty minutes at 150° before being submitted to examination at 96°, exhibited for some time a diminution in volume at this temperature, but later the volume showed a steady increase. From observations of this kind, it is inferred that, at 96°, metallic antimony consists of a mixture of at least three allotropic forms.

H. M. D.

Reduction of the Oxides of Antimony and Bismuth by their Sulphides. W. R. SCHOELLER (*J. Soc. Chem. Ind.*, 1915, **34**, 6—9).—Mixtures of antimony sulphide (Japanese stibnite) and antimony tri- or tetra-oxide (not antimonious oxide) are heated to incipient fusion or at a higher temperature (965°) in a porcelain boat in a current of dry carbon dioxide. The Sb_2O_3 in the residue is extracted by 5% tartaric acid, and is estimated iodometrically. The sulphur dioxide evolved is oxidised by a solution of iodine, and is estimated in the usual manner. Metallic antimony is produced, the best yield being obtained by heating the sulphide and trioxide (1 : 2 mol.) at 965°, but the process has the disadvantage that both antimony sulphide and trioxide volatilise in the current of carbon dioxide. Reduction to the metal does not occur when the mixtures are fused beneath sodium chloride in a crucible. Antimony is produced when stibnite alone is heated gently in a current of air, and subsequently at about 950° in a current of carbon dioxide.

The observations recorded above are briefly discussed in connexion with the metallurgy of antimony.

The oxide and the sulphide of bismuth react readily, either in a current of carbon dioxide or beneath sodium chloride in a crucible. Sulphur dioxide is evolved at a comparatively low temperature, and globules of metallic bismuth are formed by heating more strongly. The yield is 90%; a small quantity of basic bismuth sulphate is also formed. C. S.

The Effect of Hydrogen on the Annealing of Gold. JOHN PHELPS (*J. Inst. Metals*, 1914, **12**, 125—132).—The temperature at which hard-rolled gold is softened by annealing is raised by hydrogen. Thus the temperature of annealing, when heating is continued for thirty minutes, is raised from 150° to about 300° by the presence of 0·02 to 0·04 part of hydrogen per thousand. The effect is destroyed by melting the gold in air or oxygen. C. H. D.

Mineralogical Chemistry.

Litharge from Zarshuran, Persia. Alexander Scott (*Min. Mag.*, 1914, **17**, 143—146).—The specimen described is from a mineral vein which has long been worked for orpiment near the Zarshuran River, in Kurdistan. It is red with a yellowish-brown streak, and is in part crystalline, with a laminated structure. The optical characters of cleavage flakes suggest orthorhombic symmetry. Analysis gave:

PbO.	CuO.	Sb_2O_3.	P_2O_5.	CO_2.	Total.	Sp. gr.
97·17	2·61	0·30	trace	trace	100·08	8·61

Red and yellow, crystalline modifications of lead monoxide have

been prepared artificially, but there is some confusion in the crystallographic descriptions of these. L. J. S.

A New Locality for Voelckerite. AUSTIN F. ROGERS (*Min. Mag.*, 1914, **17**, 155—162).—Careful determinations of the amount of water present in apatites which are deficient in fluorine and chlorine prove that these elements are replaced isomorphously by oxygen rather than by hydroxyl, the general formula of minerals of the group being $3Ca_3(PO_4)_2,Ca(F_2,Cl_2,O,CO_3)$. For members of the group in which the oxygen atom predominates, the author has proposed the name voelckerite (A., 1912, ii, 565). The following analysis, by G. W. Jordan, is given of voelckerite from a metamorphic glaucophane-bearing rock from Calaveras Valley, Santa Clara Co., California. The mineral is white and subtranslucent, with an imperfect cleavage and faint lustre, D 3·06. Deducting a portion of the carbon dioxide as present in admixed calcite, the amount of CO_3 is calculated as 0·35 and the excess of oxygen as 1·49%:

CaO.	Al_2O_3.	FeO.	P_2O_5.	H_2O.	CO_2.	Insol.	Total.
54·46	1·35	0·24	41·47	0·22	1·03	0·53	99·30

L. J. S.

Pintadoite and Uvanite, Two New Vanadium Minerals from Utah. FRANK L. HESS and WALDEMAR T. SCHALLER (*J. Washington Acad. Sci.*, 1914, **4**, 576—579).—Pintadoite occurs as a thin, green efflorescence on the sandstone cliffs of Cañon Pintado, San Juan Co., Utah. Under the microscope, it is slightly pleochroic, and has moderate to high birefringence. It dissolves slowly in cold water. Analysis I gives the formula $2CaO,V_2O_5,9H_2O$:

	UO_3.	CaO.	MgO.	K_2O.	V_2O_5.	P_2O_5.	As_2O_5.	H_2O.	Insol.	Total.
I.	—	22 6	—	—	42·4	—	—	35·0	—	100·0
II.	39·60	1·73	0·04	0·30	37·70	0·06	0·05	18·28	1·24	99·00

Uvanite occurs as a brownish-yellow powder disseminated in sandstone at Temple Rock, Emery Co., Utah. It resembles carnotite in appearance and mode of occurrence, but it has not the clear yellow colour characteristic of carnotite. Under the microscope, the minute, crystalline particles show a high birefringence. The mineral is not soluble in water, but it dissolves very quickly in ammonium carbonate solution. Analysis II agrees with $2UO_3,3V_2O_5,15H_2O$. L. J. S.

Barkevikite from Lugar, Ayrshire. ALEXANDER SCOTT (*Min. Mag.*, 1914, **17**, 138—142).—Black, lustrous, prismatic crystals of barkevikite occur in a rock called lugarite. The optical characters are in agreement with those of the original barkevikite from Barkevik, in Norway. D 3·298; analysis gave:

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.	Na_2O.	K_2O.	H_2O.	Total.
42·48	2·90	8·58	6·81	15·62	0·39	2·78	13·45	6·32	0·60	0·25	100·18

The relation of barkevikite to other members of the amphibole group is discussed. L. J. S.

Meteorites of Uwet and Angela: Re-determination of Nickel and Iron in the Baroti and Wittekrantz Meteoric Stones. G. T. PRIOR (*Min. Mag.*, 1914, **17**, 127—134).—A mass of iron, weighing about 55 kilos., fell about ninety years ago at Uwet, in Southern Nigeria. An etched slice shows well-marked Neumann lines, together with needles of schreibersite and nodules of troilite. The iron belongs to the normal hexahedrite group of the type of Braunau. Analysis I corresponds with $Fe_{14}Ni$.

Several masses of iron, the largest weighing 4341 grams, have been found embedded in the caliche at the Angela Nitrate Works, near Santa Catalina, Iquique, Chili. This iron is an ataxite containing a comparatively low percentage of nickel (anal. II), and characterised by its extraordinary richness in schreibersite (amounting to nearly a quarter of the mass); it is probably identical with La Primitiva (A., 1898, ii, 391):

	Fe.	Ni.	Co.	Cu.	P.	C.	Total.	Sp. gr.
I.	93·36	5·78	0·75	nil	0·25	0·03	100·17	7·862
II.	95·03	4·52	0·65	—	trace	trace	100·20	7·892

The separation of iron and nickel by means of ammonia is found to be incomplete even after several precipitations. Triple precipitation of the iron with sodium acetate, and subsequent precipitation with ammonia, gives more accurate results; the percentages previously given for the Baroti and Wittekrantz meteorites (A., 1914, ii, 64) are now corrected. L. J. S.

Analytical Chemistry.

Regulator Mixtures, Recent Indicators, etc. GEORGE STANLEY WALPOLE (*Biochem. J.*, 1914, **8**, 628—639).—The diagram presented in a previous paper (A., 1910, ii, 995) has been modified by the inclusion of the data for a number of indicators referred to in the recent literature. Amongst these, reference may be made to 2 : 5-dinitroquinol, which is of especial interest in that it gives at a glance the approximate reaction of any solution for which P_H lies between 3 and 9·5 ($c_H=10^{-3}$ and $10^{-9\cdot5}$). Over this range, the indicator shows a steady change of colour. In dilute acid solutions it is green, and assumes a yellowish tinge at $P_H=3$. In neutral solution ($P_H=7$) it is bright reddish-brown, and at $P_H=9\cdot5$ a purple tint is reached, which undergoes no change on further addition of alkali. The change from green to brown is very sharp at $P_H=3\cdot4$ to $4\cdot7$, and so is that from brown to purple in the region $P_H=8\cdot3$ to $9\cdot3$.

The results obtained in recent measurements of the hydrogen-ion concentration of regulator mixtures, including acetic acid + sodium acetate, hydrochloric acid + sodium acetate, and cacodylic acid + sodium cacodylate, are also incorporated in the new chart.

Incidentally, it has been found that phenolphthalein reacts quite normally as an indicator of the hydrogen-ion concentration even in solutions containing ammonia. Solutions containing (1) sodium dihydrogen borate, (2) ammonium chloride + sodium hydroxide, which gave the same tint with phenolphthalein, were found to have the same hydrogen-ion concentration as measured by the hydrogen electrode method. H. M. D.

Estimation of Hydrogen in Gas Mixtures by means of Colloidal Palladium. G. A. BURRELL and G. G. OBERFELL (*J. Ind. Eng. Chem.*, 1914, **6**, 992—994).—Results are recorded of the use of Paal and Hartmann's method (A., 1910, ii, 237) for estimating hydrogen; the method was found to be trustworthy. W. P. S.

Method for Estimating the Critical Moisture Content of Soils. R. O. E. DAVIS (*J. Ind. Eng. Chem.*, 1914, **6**, 1008—1010).—The critical moisture content corresponds with that physical condition of the soil when it is most suited for plant growth and for cultivation. The air-dried soil is ground in a mortar just sufficiently to break up any lumps, and is then filled into a brass tube about 1 foot long and 1 inch in diameter; a slit is cut in this tube about half an inch wide, and extending almost the whole length of the tube, and a strip of celluloid placed over the slit forms a kind of window. The lower end of the tube is covered with a piece of cloth, and the tube is tapped until the soil column becomes so solid that the top does not break when the tube is placed in a horizontal position. The tube is then placed in water until the soil column becomes wet an inch or more above the water-level; it is then removed from the water, the wet end is covered with a piece of sheet rubber to prevent evaporation, and placed in a horizontal position for eighteen hours. The length of the soil column should be such that the dry soil beyond the point to which the moisture has advanced is at least 2 inches. The tube is now opened, and the moisture estimated in a sample taken from the first inch of moist soil next to the dry portion. This moisture content represents the critical moisture content of the soil.

W. P. S.

Very Sensitive Reaction for Hydrogen Peroxide. A. ROGAI (*Ann. Chim. Applicata*, 1914, **2**, 341; from *Staz. sperim. agrar. ital.*, 1914, **67**, 569).—Two or three drops of freshly prepared ferrous sulphate solution, a few drops of potassium thiocyanate solution, and 5—6 c.c. of ether are mixed in a test-tube. A small amount of the liquid to be tested for the presence of hydrogen peroxide is then shaken with the mixture, the ether assuming a colour ranging from pale red to blood-red, according to the content of the peroxide. One-tenth of a c.c., containing 0·0000144 gram of hydrogen peroxide, gives a sharp reaction.

The ether employed should be as pure as possible and free from oxidation products formed by the action of light. It may be prepared by shaking the ether with ferrous sulphate solution and dis-

tilling from the latter, and is best stored in a coloured bottle in contact with aqueous ferrous sulphate. T. H. P.

Simple and Accurate Method for the Estimation of Chlorides in Albuminous Liquids. C. GAZZETTI (*Arch. di Fisiol.*, 1914, **11**, 81—88; from *J. Soc. Chem. Ind.*, 1914, **33**, 1173).—A small, measured quantity of the liquid is diluted with water in a 100 c.c. flask, 3 c.c. of 50% ferric alum are added, the precipitated ferric albuminate is dissolved by the addition of concentrated nitric acid drop by drop, and a measured excess of $N/50$-silver nitrate is added to the clear solution; the colloidal matter in the solution prevents the precipitation of silver chloride. The mixture is diluted with water to about 97 c.c., and is then made up to the mark by the addition of concentrated nitric acid. This causes the flocculation of the albumin and the precipitation of silver chloride. The whole is filtered, and in 50 c.c. of the clear filtrate the excess of silver nitrate is estimated by titration with $N/50$-potassium thiocyanate. C. S.

New Apparatus for Use in the Winkler Method for Oxygen Dissolved in Water. HYMAN L. SHOUB (*U.S. Hyg. Labor., Bull.*, No. 96, 83—85).—An apparatus consisting of a 200 c.c. pipette and a pressure regulator has been designed whereby the water which has been prepared for titration in Winkler's method can be automatically drawn into the pipette and maintained there indefinitely without contact with the air. By opening a stopcock, 200 c.c. of the water are rapidly discharged into any desired receptacle. C. S.

Comparison of Methods for the Determination of Oxygen in Waters in the Presence of Nitrites. ELIAS ELVOVE (*U.S. Hyg. Labor., Bull.* No. 96, 15—35).—Experimental data are recorded in support of the following statements. Levy's method of estimating the oxygen dissolved in water containing nitrites is untrustworthy. Hale and Melia's potassium acetate modification of Winkler's method gives accurate results when the following precautions are observed. In the presence of a considerable amount of nitrite, the results may be too high if there is not a sufficiently long period intervening between the addition of the potassium acetate and the titration of the iodine. At 20°, with a water containing 5 parts of nitrite per million, the proper interval is fifteen minutes. Hale and Melia's explanation of the counteracting effect of the acetate on the nitrite interference is insufficient in view of the fact that an acetic acid medium does not prevent these interferences. The rôle of the potassium acetate is to diminish the concentration of the hydrogen ions, and an excess of the salt, therefore, is essential.

The permanganate modification of Winkler's method, since it is applicable in the presence of nitrites and organic matter, is preferable to the acetate modification, which counteracts only the interference from nitrites. In carrying out the permanganate modification in bottles of about 270 c.c. capacity, each bottle should con-

tain not less than 0·45 gram of potassium iodide, and the amount of the excess of potassium oxalate should not be more than 1 c.c. of the 1% solution. C. S.

Estimation of Sulphur in Rubber. R. GAUNT (*Analyst*, 1915, **40**, 9—11).—The following method is recommended for the estimation of sulphur in caoutchouc and vulcanised materials by direct combustion in oxygen and absorption of the resulting sulphur dioxide; the procedure described prevents the formation of any volatile products which may escape combustion. From 0·2 to 0·3 gram of the sample is placed in a small hard-glass tube, closed at one end, and this is inserted into the centre of a combustion tube about 35 cm. long. One end of the combustion tube is drawn out and connected with two small absorption flasks, each containing 25 c.c. of 20 vol. hydrogen peroxide; a plug of platinised asbestos is placed in this end of the tube. The tube is heated by a burner, while a current of dry oxygen is passed through the apparatus, the residual mass being strongly heated towards the end of the combustion; any carbon deposited on the inner surface of the tube or on the asbestos is burnt by moving the burner along the tube. The sulphur dioxide collected in the absorption flasks may be estimated gravimetrically or by titration with standard alkali solution. In the case of caoutchouc containing much mineral matter, the sulphates in the residual ash must also be estimated. The results obtained by the method agree with those yielded by the Carius process. W. P. S.

Lime-Sulphur Sprays, their Composition and Analysis. A. A. RAMSAY (*J. Agric. Sci.*, 1915, **6**, 476—483.* Compare *ibid.*, 194).—Calcium disulphide occurs in lime-sulphur solution in addition to the compounds previously mentioned—calcium hydroxyhydrosulphide, thiosulphate and sulphate, and sulphur. The method of analysis is as follows. The concentrated solution (50 c.c.) is first diluted to 500 c.c. Of this, 25 c.c. are titrated with $N/10$-iodine until the yellow colour is discharged. The number of c.c. used × 0·0016 and by 0·0028 gives the amount of sulphur and lime respectively. The titration is then continued until there is a tinge of yellow. The number of c.c. used × 0·0064 and 0·0056 give, respectively, the sulphur and the calcium as thiosulphate.

The titrated solution is next filtered, and the sulphur, as sulphate and sulphite, estimated with barium chloride.

Another 10 c.c. of the diluted solution is further diluted with about 25 c.c. of water and twice extracted, in the usual manner, with 10 c.c. of carbon disulphide. The weight of the residue obtained, dried at 70° or less, is that of the free sulphur.

The total sulphur is estimated in another 10 c.c., to which 6—8 grams of sodium peroxide are added. After a few minutes water (50—75 c.c.) is added, and then hydrochloric acid until clear. After adding a few drops of a 15% solution of potassium iodide, the solution is boiled, diluted to 200 c.c., and precipitated with barium chloride.

* and *J. Roy. Soc. New South Wales*, 1914, **48**, 242.

The total calcium is estimated in 10 c.c. of the diluted solution, in the usual manner, after decomposing the sulphides and thiosulphates with $N/10$-iodine solution, and filtering off the sulphur.
N. H. J. M.

Estimation of Nitrogen in Steel. L. E. Barton (*J. Ind. Eng. Chem.*, 1914, **6**, 1012—1013).—When the nitrogen in steel is converted into ammonia, and this estimated colorimetrically by Nessler's reagent, it sometimes happens that the test solution and the comparison solution yield different colorations with the reagent; there is also a tendency for the solutions to become turbid. These difficulties may be overcome by adopting the following procedure, the essential point being the preparations of the test and comparison solutions under exactly similar conditions. Forty c.c. of sodium hydroxide solution and 500 c.c. of water are placed in a flask and distilled until the distillate no longer gives a coloration with Nessler's reagent. Five grams of the sample of steel are then dissolved in hydrochloric acid, the solution is added to the contents of the flask and distilled, 150 c.c. of distillate being collected. Twenty-five c.c. of standard ammonium chloride solution are then added to the flask and distilled, 150 c.c. of distillate also being collected in this case. These two distillates are employed in the colorimetric estimation of the ammonia. W. P. S.

Kjeldahl Distillation Apparatus. Arthur D. Holmes (*J. Ind. Eng. Chem.*, 1914, **6**, 1010—1012).—An apparatus is described for making ten or more distillations at one time; the bank of condensers is so arranged that each is entirely separate, and may be removed without interrupting the action of the others. The water supply to each condenser is regulated by separate taps, as is the gas supply to the burners under the distillation flasks. W. P. S.

Modification of Kjeldahl's Method for the Estimation of Nitrogen in Organic Substances. Max Wunder and Octavien Lascar (*Ann. Chim. anal.*, 1914, **19**, 329—332).—From 0·1 to 0·6 gram of the substance, according to its nitrogen-content, is placed in a flask, together with 3 grams of oxalic acid, 2 grams of sodium oxalate, and 0·5 gram of vanadium pentoxide; a mixture consisting of 5 c.c. of phosphoric acid (D 1·71) and 25 c.c. of sulphuric acid is added, and the contents of the flask are heated gradually until the colour changes from black to greenish-yellow. After cooling, 100 c.c. of water and about 0·75 gram of fine iron wire are added, the solution is heated for about thirty minutes, and the ammonia is then estimated by distillation. When the nitrogen in the substance is in combination with oxygen, it is necessary to introduce iron wire before and after the digestion with the acid mixture. W. P. S.

Detection of White Phosphorus in Matches. Earle B. Phelps (*U.S. Hyg. Labor., Bull.* No. **96**, 51—54).—Thorpe's method (T., 1909, **95**, 440) for the qualitative separation of white phos-

phorus in matches gives satisfactory results, but is not sufficiently sensitive for the detection of small quantities and is not sufficiently rapid for the examination of a large number of samples. The author's method, which is based on the volatility of white phosphorus with steam and its luminescence in contact with oxygen, detects 0·1 mg. suspended in 10 c.c. of water. In a specially designed apparatus, which is figured and described, a current of hydrogen is washed by alkaline pyrogallol, and then is passed through a small jet into boiling water in a test-tube containing ten or twelve match-heads. The gas issues through a fine capillary at a relatively high velocity (under these conditions the intensity of the glow is increased). The capillary is enclosed in a dark chamber, and is viewed through a small microscope. The upper two inches of the capillary are heated electrically to prevent condensation, but this, and also the washing of the hydrogen, are refinements which are not necessary in the case of ordinary phosphorus matches. The method is applicable in the presence of nitrates, chlorates, hydrogen sulphide (from the so-called phosphorus sesquisulphide in matches), or carbon disulphide. C. S.

The Gravimetric Estimation of Minute Quantities of Phosphorus. Henry Stanley Raper (*Biochem. J.*, 1914, **8**, 649—655).—A method is described for the gravimetric estimation of quantities of phosphorus as low as 0·1 mg. It is a modification of Ibbotson and Brearley's method for the estimation of phosphorus in steel (A., 1900, ii, 757; 1901, ii, 343). After preliminary oxidation to phosphoric acid, the phosphorus is precipitated under special conditions as ammonium phosphomolybdate. The molybdenum in this is then estimated as lead molybdate. The method is rapid and accurate. W. D. H.

Strength of Nitric Acid, Period of Extraction, and Ignition as Affecting the Gravimetric Estimation of Phosphoric Acid in Soils. O. L. Brauer (*J. Ind. Eng. Chem.*, 1914, **6**, 1004—1005).—All the soluble phosphoric acid is extracted from a soil by nitric acid when the strength of the latter is not less than $2N$; the extraction need not be continued for a longer period than two hours on a steam-bath. The quantity of phosphoric acid soluble in nitric acid decreases when the soil is ignited before being extracted; the decrease may amount to 0·026% of P_2O_5 after one hour's ignition at a red heat. W. P. S.

Blood-Charcoal as a Purifying Agent for Arsenic Solutions Previous to Titration. Robert M. Chapin (*J. Ind. Eng. Chem.*, 1914, **6**, 1002—1003).—Blood-charcoal may be used for decolorising such solutions as used sheep-dip liquids before the arsenious acid present is titrated with iodine solution. The charcoal absorbs a small quantity of the arsenious acid; this quantity is recovered when the charcoal is washed, not, however, as arsenious acid, but as arsenic acid. The absorption is proportional to the weight of the charcoal employed, and, in the estimation of arsenious acid, a correction is

applied for this quantity as estimated under the conditions obtaining in the analysis. W. P. S.

Estimation of Mixtures of Argon and Nitrogen by the Aid of Liquid Air. L. HAMBURGER and H. FILIPPO, JUN. (*Chem. Weekblad*, 1915, **12**, 2—6).—A description of a type of differential vapour-tension thermometer adapted to the analysis of argon employed in the manufacture of half-watt lamps. The sample under investigation is cooled with liquid air, and its vapour tension compared with that of a sample of pure argon under the same conditions. A. J. W.

Estimation of Radium. H. SCHLUNDT (*Met. and Chem. Eng.*, 1914, **12**, 709—710; from *J. Soc. Chem. Ind.*, 1914, **33**, 1173).—In the emanation method, which consists in introducing the emanation from the ore into a standardised, air-tight electroscope or an ionisation vessel connected with an electrometer, the solution method (fusion with mixed alkali carbonates, followed by solution and boiling) of obtaining the emanation from rocks, etc., which do not dissolve in hot acids, gives only 70—80% of the values obtained by the fusion method. The latter consists in fusing the sample with a suitable flux, such as the mixed alkali carbonates, in a closed, electrically heated furnace; the liberated emanation is freed from carbon dioxide and collected.

Fusion with the mixed alkali carbonates is better than with potassium hydrogen sulphate, except in the case of carnotite. Borax as flux gives low results. The emanation is separated completely from uranite by solution in nitric acid and by fusion with ordinary fluxes. C. S.

Titration of Silver in Argentum Colloidale and Argentum Proteinicum. A. KORNDÖRFER (*Pharm. J.*, 1914, **93**, 809; from *Apoth. Zeit.*, 1914).—*Argentum Colloidale*: 0·2 gram of the substance is dissolved in 5 c.c. of water, 5 c.c. of dilute sulphuric acid are added, the solution is heated slightly, and then boiled, with the addition of 10 c.c. of 3% hydrogen peroxide solution, until colourless. After cooling, 50 c.c. of water are added, and the solution is titrated with $N/10$-thiocyanate solution in the usual way. *Argentum Proteinicum*: 0·5 gram of the substance is heated with 5 c.c. of water and 5 c.c. of dilute sulphuric acid; 15 c.c. of 3% hydrogen peroxide solution are then added, and the mixture is boiled until the colour of the solution is yellow. The cooled solution is diluted with 100 c.c. of water, and titrated with $N/10$-thiocyanate solution. W. P. S.

Estimation of Peroxide in Commercial Lead Oxide. L. S. DEAN (*Chem. News*, 1915, **111**, 2).—A method described by Andrews (A., 1903, ii, 682), in which the peroxide is decomposed by hydrochloric acid in the presence of potassium iodide, and the excess of the latter titrated back with potassium iodate solution, using chloroform or carbon tetrachloride as the indicator, was found to be trust-

worthy. The results obtained agreed with those yielded by the Bunsen method. W. P. S.

Volumetric Estimation of Copper in its Salts and in many of its Alloys. G. Zuccari (*Ann. Chim. Applicata*, 1914, **2**, 287—290; *Boll. Chim. Farm.*, 1914, **53**, 321—323).—Copper may be readily estimated by titration with a standard sodium nitroprusside solution, the reaction being expressed by the equation

$$Na_2Fe(CN)_5NO + CuSO_4 = Na_2SO_4 + CuFe(CN)_5NO.$$

If the sodium nitroprusside solution contains 46·866 grams of the crystallised salt ($+2H_2O$) per litre, each c.c. corresponds with 0·01 gram of copper. When the liquid has almost lost its blue colour, a drop is filtered through a thin, tight filter paper, and yellow ammonium sulphide solution brought into contact with the paper immediately surrounding the drop. If copper is still present in appreciable proportion in the filtrate, a brownish coloration is formed, but with minimal traces of copper only the yellow colour of the ammonium sulphide is seen. Excess of sodium nitroprusside gives, on the other hand, a violet coloration, which rapidly disappears when the excess is very slight.

This method is applicable to commercial copper salts containing salts of iron, zinc, metals of the alkaline earths, etc. The iron should be oxidised to the ferric state by boiling the solution with nitric acid, the cold liquid being then titrated in the manner described above, since free nitric acid does not affect the reaction. Zinc salts are without influence at low concentrations, 50 grams of zinc sulphate per litre being necessary to disturb the titration. Sodium nitroprusside does not precipitate the metals of the alkaline earths, manganese, aluminium, tin, lead, etc. The method may also be used for the estimation of copper in alloys free from cadmium and nickel, but the concentration of the solution of the alloy should not exceed 2—3%. It serves likewise for the estimation of alkali nitroprussides.

If stored in the dark in a bottle of non-alkaline glass fitted with a ground stopper, the sodium nitroprusside solution remains unaltered for months; faint acidification, for instance, with sulphuric acid increases the stability of the liquid against the effects of alkaline glass and of light. T. H. P.

Volumetric Estimation of Mercury. J. E. Clennell (*Eng. and Mining J.*, 1914, 787—789; from *J. Soc. Chem. Ind.*, 1914, **33**, 1173).—Mercury is rapidly and accurately estimated by precipitating the hydroxide by an excess of sodium hydroxide, dissolving the precipitate in a measured quantity of standard potassium cyanide, and titrating the excess of the latter with standard silver nitrate; potassium iodide serves as an indicator, the end-point being denoted by the appearance of a yellow turbidity: (1) $HgO + 4KCN + H_2O = K_2Hg(CN)_4 + 2KOH$; (2) $K_2Hg(CN)_4 + AgNO_3 = Hg(CN)_2 + KAg(CN)_2 + KNO_3$.

Samples containing mercurous salts can usually be completely dissolved by a preliminary treatment with saturated bromine water.

The excess of bromine must be completely expelled by boiling before the sodium hydroxide is added. Other metals, such as copper, nickel, or zinc, which react with potassium cyanide, can be readily eliminated by utilising the insolubility of mercuric sulphide in moderately concentrated nitric acid. The presence of iron obscures the end-point. The iron is oxidised to the ferric state by boiling with nitric acid before the addition of sodium hydroxide; after the standard potassium cyanide has been added, the ferric hydroxide is removed by filtration.

To obtain accurate results, a large excess of potassium cyanide must be avoided. A moderate excess of alkali does not affect the result. The loss of mercury salt on boiling the solution for thirty seconds is negligible. C. S.

Rapid Estimation of Iron in Industrial Pyrophoric Alloys (Iron-Cerium Alloys). I. Bellucci (*Ann. Chim. Applicata*, 1914, **2**, 366—369).—The automatic pocket lighters now so largely used contain an alloy of iron with metals of the cerium group, small proportions of aluminium, manganese, zinc, copper, lead, antimony, magnesium, silicon, phosphorus, and carbon being present as impurities. The iron present may be estimated as follows: 0·2—0·3 gram of the alloy is dissolved at the ordinary temperature in a small quantity of concentrated hydrochloric acid, gaseous hydrocarbons being evolved, and a little carbon and silicon deposited. Hydrogen sulphide is passed through the slightly diluted and gently heated acid solution. The filtered liquid is heated in a porcelain basin on a water-bath until free from hydrogen sulphide, 5—10 c.c. of 3% hydrogen peroxide solution being afterwards added to the liquid, which is then evaporated to dryness. The residue is extracted with water faintly acidified with hydrochloric acid, and the iron in the solution thus obtained estimated iodometrically. T. H. P.

Estimation of Cobalt in High-speed Steels. Lawrence Dufty (*J. Iron Steel Inst.*, 1914, **90**, 52—65).—Neither the cyanide nor the nitrite method gives good results in the estimation of cobalt in high-speed steels. The best results are obtained by the following method.

Three grams of steel drillings are dissolved in 50 c.c. of concentrated hydrochloric acid, oxidised with a very slight excess of nitric acid, and evaporated to a syrup with another 20 c.c. of hydrochloric acid. After mixing with 5 volumes of 5% hydrochloric acid, it is filtered through pulp, the tungstic acid being washed with dilute hydrochloric acid. The filtrate is exactly neutralised with ammonia and ammonium carbonate while hot, 20 c.c. of 33% acetic acid are added, and the boiling solution precipitated with ammonium acetate, boiled, made up to 750 c.c., and 500 c.c. filtered through a dry filter. The precipitate contains the whole of the chromium, molybdenum, and vanadium with the iron. All cobalt, nickel, and manganese are left in the filtrate.

Any small quantity of iron is removed from the filtrate by adding 5 c.c. of hydrochloric acid, evaporating to small bulk, and pre-

cipitating with ammonia. This precipitation must be repeated. The united filtrates are neutralised with acetic acid, adding 4 c.c. in excess, and 15 c.c. of ammonium acetate solution. Cobalt is precipitated by passing a rapid stream of hydrogen sulphide for fifteen minutes. The sulphide is washed with water containing ammonium acetate, and manganese may be estimated in the filtrate.

The cobalt sulphide is dissolved in nitric acid, any residue being ignited, dissolved, and added. The solution is mixed with 20 c.c. of hydrochloric acid, and, after evaporating to 10 c.c., is diluted and precipitated by adding 1 gram of ammonium phosphate and just enough ammonia to give a slight precipitate in the hot solution, followed by 15 c.c. of ammonium acetate, after which ammonia is added drop by drop until faintly alkaline. On stirring, the flocculent, blue precipitate becomes pink and crystalline, and is ready for filtration after fifteen to twenty minutes on the water-bath. The ammonium cobalt phosphate is ignited to pyrophosphate. A minute quantity of cobalt remains in the filtrate, and may be recovered by means of hydrogen sulphide. Manganese is then estimated in the filtrate.

Nickel, if present, is separated by means of dimethylglyoxime after the acetate separation. The excess of dimethylglyoxime is removed by nitric acid before precipitating cobalt. C. H. D.

A Sensitive Test for Chromates. P. N. VAN ECK (*Chem. Weekblad*, 1915, **12**, 6—8).—Addition of a trace of α-naphthylamine to a solution of potassium dichromate, and acidification of the mixture with tartaric acid, produces an intense blue coloration. The reaction is applicable to the colorimetric estimation of chromates. A. J. W.

Electrolytic Method of Precipitating Tin. L. HUMPHREVILLE (*Eng. and Min. J.*, 1914, **98**, 964; from *J. Soc. Chem. Ind.*, 1914, **33**, 1228).—The tin, weighing from 0·2 to 0·3 gram, is separated as its sulphide; this is dissolved in 16 c.c. of ammonium sulphide, 20 c.c. of 40% sodium sulphite solution are added, the solution is diluted to 120 c.c., and electrolysed at 60° with a current of 5·5 amperes at 4 volts. Cylindrical gauze electrodes are used, and the electrolyte is agitated by a stirrer making 600 revolutions per minute; the deposition of the metal is completed in twenty-five minutes. Before use, the platinum cathode is coated with copper and tin in succession, or with cadmium alone. Impurities present in ordinary ammonia solution interfere with the accuracy of the method; the ammonium sulphide should, therefore, be prepared by saturating with hydrogen sulphide an ammonia solution (D 0·91) obtained by dissolving ammonia gas in water. The sodium sulphite is employed to render the tin solution colourless. W. P. S.

Estimation of Vanadium in Ferro-Vanadium and Steel. O. WILMS and P. FISCHBACH (*Stahl und Eisen*, 1914, **34**, 417—418).—The method of evaporating a solution of the metal in nitric acid with hydrochloric acid, and titrating the oxychloride with potassium

permanganate in presence of phosphoric acid at 80—85°, gives low results, owing to the volatility of the oxychloride. This may be avoided by evaporating with sulphuric acid until fumes are produced, in order to convert the oxychloride into the non-volatile oxysulphate. C. H. D.

Detection of the Substitution of Denatured Alcohol for Rectified Alcohol. F. Richard (*J. Pharm. Chim.*, 1914, [vii], **10**, 429—437).—The test proposed depends on the presence of acetone in denatured alcohol, and the detection of this constituent by means of the iodoform reaction. Alcohol and acetaldehyde also give the iodoform reaction, but the iodoform formation is slow, whilst with acetone the reaction takes place immediately. One part of acetone in 10,000 parts may be detected by the test. Denatured alcohol also decolorises potassium permanganate solution, but rectified alcohol does so only after some lapse of time. The iodoform test may be used for the detection of denatured alcohol in tinctures, essences, etc., after any essential oils which may be present have been removed by shaking the diluted sample with ether. W. P. S.

Physical Chemistry Applied to Wine. C. Mensio and E. Garino-Canina (*Ann. Chim. Applicata*, 1914, **2**, 315—340).—From the results of their experiments, and the consideration of those obtained by previous investigators, the authors draw the following general conclusions. In all wines, the strong acids present must be regarded as completely combined, and the weak, organic acids as partly free and partly combined. Further, the combined tartaric acid, for example, is united with various bases, and not solely with potassium, so that the official estimation of the hydrogen tartrate and of the free tartaric acid is valueless. The acidity of wine is characterised best by the hydrogen-ion concentration, and the acidities of the wines examined are comparable with those of $N/1000$—$N/3000$-hydrochloric acid. The concentration of the hydrogen ions serves in the calculation of the free and combined proportions of the various acids. Valuable information is furnished also by the curve representing the variation in electrical conductivity of a wine the acidity of which is gradually neutralised with baryta, the character of the variation depending on the phosphates, the strong and weak acids and bases, etc. From a knowledge of the constituents of the ash, the proportions of each acid combined with the different bases may be deduced. T. H. P.

Estimation of Sucrose in the Molasses of Beetroots. Method of Inversion by Neutral Double Polarisation. Émile Saillard (*Compt. rend.*, 1915, **160**, 31—34).—In order to avoid the errors due to the presence of active nitrogenous substances and of salts in the molasses, the author suggests the following procedure for determining the percentage of sucrose in the molasses of beetroots.

Four times the French normal weight of neutralised molasses are put into a 200 c.c. flask, defecated with just sufficient basic lead

acetate, the liquid made up to 200 c.c., and filtered (filtrate K). To 50 c.c. of this filtrate, potassium chloride, just equivalent to the hydrochloric acid to be used for inversion, is added, the solution made up to 100 c.c., shaken with a little purified animal charcoal, filtered, and polarised at 20° (reading A). A second 50 c.c. of K are inverted with 6·8 c.c. of hydrochloric acid (22° B), neutralised with potassium hydroxide, cooled to 20°, made up to 100 c.c., clarified with animal charcoal, and polarised at 20° (reading B). Then the percentage of sucrose equals

$$100(A+B)/(\text{coefficient of inversion} - \tfrac{1}{2}t).$$

The coefficient of inversion is determined as follows. The amount of hydrochloric acid equivalent to the sulphuric acid in the sulphated ashes of the French normal weight of molasses is calculated. Suppose it to be 1·8 c.c. of acid (D 1·18). A pure sucrose solution (P) of the same polarisation as the filtrate K above is prepared. Fifty c.c. of this solution P are taken, and there is added potassium chloride equivalent to 8·6 c.c. of hydrochloric acid (D 1·18); this is made up to 100 c.c., shaken, and polarised at 20° (reading A'). To 50 c.c. of P, 5 c.c. of hydrochloric acid (D 1·18) are added, mixed, inverted, cooled, 3·6 c.c. of hydrochloric acid added, neutralised with potassium hydroxide, made up to 100 c.c., shaken, and polarised at 20° (reading B'). Another 50 c.c. of P are taken, diluted to 100 c.c., shaken, and polarised at 20° (reading A''). Then the coefficient of polarisation equals

$$[100(A'+B')+\tfrac{1}{2}tA'']/A''.$$

The results obtained by this method are about 1·5% higher than those obtained by the usual Clerget method, but are the same as those obtained by Bertrand's method after inversion and defecation. W. G.

Hydrolysis of Maltose by Hydrochloric Acid under the Herzfeld Conditions. WILLIAM A. DAVIS (*J. Agric. Sci.*, 1915, **6**, 413—416).—A reply to Kluyver (*Biochem. Suikerbepal.*, 1914). When heated with hydrochloric acid under Herzfeld conditions, maltose undergoes slight hydrolysis, amounting to about 2% in 1% solutions. When maltose is likely to be present, it is, therefore, preferable to employ 10% citric acid. N. H. J. M.

Estimation of Carbohydrates. IV. Presence of Free Pentoses in Plant Extracts and the Influence of Other Sugars on Their Estimation. WILLIAM A. DAVIS and GEORGE CONWORTH SAWYER (*J. Agric. Sci.*, 1915, **6**, 407—412).—Pentoses were found, and estimated, in the leaves of a number of plants, such as mangolds, turnips, carrot, potato, etc. The amount can be estimated in the usual manner, or by the reducing power after fermentation. When the amounts of pentoses are small, large amounts of other sugars being present, it is desirable to ferment the solutions before using the distillation method. N. H. J. M.

New Reaction for Salicylic Acid. PARIDE TORTI (*Boll. Chim. Farm.*, 1914, **53**, 400).—When heated with a drop of nitric acid

(D 1·40), a crystal of salicylic acid dissolves, giving a yellow coloration. Even without heating, a vigorous reaction commences after some time, with development of heat and liberation of nitrogen peroxide; subsequently, the reaction proceeds slowly, with evolution of colourless gas bubbles. After the liquid has cooled, minute, shining, lemon-yellow crystals separate, which dissolve in water, alcohol, or ether, forming yellow solutions. The latter give an intense red coloration with aqueous 1% ferric chloride solution, the sensitiveness of this reaction being similar to that between ferric chloride and salicylic acid. The yellow colour of the above aqueous, alcoholic, or ethereal solution becomes intensified to orange on addition of sodium hydroxide solution, subsequent introduction of an acid being followed by gradual return of the original yellow colour. T. H. P.

Estimation of "Saccharin" and of Sodium *o*-Sulphonylaminobenzoate. U. Pazienti (*Ann. Chim. Applicata*, 1914, **2**, 290—294).—Glückmann's method of estimating "saccharin" (A., 1901, ii, 588) assumes the absence of impurities other than *p*-sulphonylaminobenzoic acid, but gives good results with "saccharin" obtained by precipitating sodium *o*-sulphonylaminobenzoate in aqueous solution by means of 6% hydrochloric acid.

The proportion of "saccharin" present in commercial sodium *o*-sulphonylaminobenzoate may be estimated as follows. An excess of 6% hydrochloric acid is added to a 10% aqueous solution of the salt ($+2H_2O$), the precipitated "saccharin" being washed on the filter with the 6% acid until free from sodium, and the filtrate evaporated to dryness; the sodium chloride in the dry residue is then estimated either gravimetrically or volumetrically, 58·5 parts of sodium chloride corresponding with 183 parts of "saccharin." Another method consists in drying the precipitated "saccharin," collected on a weighed filter and washed as described above, at 60° until no further loss in weight occurs; in this case, however, the solubility of the "saccharin" must be allowed for by increasing the weight found by 0·0403 gram per 100 c.c. of total filtrate and washing liquid.

In sodium *o*-sulphonylaminobenzoate, shown by qualitative tests to be pure, the "saccharin" may be estimated by titrating a neutral solution of the salt with standard silver nitrate solution in presence of a few drops of potassium chromate until the colour of silver chromate appears in the liquid. With a particular sample of sodium *o*-sulphonylaminobenzoate, this volumetric method gave 81·94% of "saccharin," the percentage of "saccharin" found by weighing being 81·78, and the calculated proportion for the pure salt, 82·06%. T. H. P.

Determination of Hübl Iodine Numbers in Alcoholic Solutions. Iodine Numbers of Essential Oils. R. Marcille (*Compt. rend.*, 1914, **159**, 1004—1007).—Determinations of the Hübl iodine numbers of essential oils in alcoholic solutions gave different results when the concentration of the alcohol or the intensity of the light

varied. In order to obtain concordant and comparable results for this iodine number, when working with alcoholic solutions, it is essential that the alcoholic concentration shall always be the same, and the reaction must be allowed to take place in the dark.

W. G.

Rate of Inactivation by Heat of Peroxydase in Milk. SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1914, **8**, 656—669).—The temperature-coefficient for the change is 2·23 per degree, a value of the same order as that for the inactivation by heat of certain lysins and for the rate of coagulation of egg albumin.

Below 70°, the rate of inactivation is so small that the peroxydase reaction cannot be utilised as a test for "pasteurisation." It may, however, indicate whether milk has been overheated. Small additions of acid retard, and of alkali accelerate, the rate. Salts retard the rate both in milk and whey, but the action is variable and independent of the valencies of their ions. In both milk and whey the reaction is one of the first order. W. D. H.

Determination of the Freezing Point of Fats. J. HARTING and J. VAN DONGEN (*Pharm. Weekblad*, 1914, **51**, 1415—1418).—For determining the freezing point of fats, and especially of fatty acids, the authors recommend the apparatus devised by Polenske (*Zeitsch. Nahr. Genussm.*, 1907, **13**, 758), but consider that his modus operandi would be improved by constant stirring of the liquid, and by taking the maximum reading of the thermometer as the freezing point. A. J. W.

Estimation of Fat in Fæces. FRANK C. GEPHART and FRANK A. CSONKA (*J. Biol. Chem.*, 1914, **19**, 521—531).—By the Liebermann-Székely method, a small amount of cholesterol is determined with the fatty acids. The Kumagawa-Suto method is laborious and difficult, and does not yield good results with pure fats or cholesteryl esters. The method proposed is easy, and gives good results; its steps are: (1) to saponify with alcoholic potash the powdered or moist material; (2) dilute with water and acidify with hydrochloric acid; (3) extract with ether and wash the ethereal extract; (4) distil off the ether and dry the fatty acids; (5) dissolve in light petroleum, filter, and titrate with $N/10$-alcoholic potash.

$$\text{Calculation, } \frac{\text{c.c. } N/10 \times 0{\cdot}0297}{\text{weight of substance}} \times 100 = \text{tristearin } \%.$$

W. D. H.

Estimation of Cineole (Eucalyptol) in Eucalyptus Oil. JOSEPH L. TURNER and RALPH C. HOLMES (*Pharm. J.*, 1915, **94**, 60—62).—Arsenic acid forms an additive product with cineole, and the reaction affords a method of estimating the latter; the compound is more stable than the similar one formed with phosphoric acid. Ten c.c. of eucalyptus oil, cooled to 0°, are mixed with 10 c.c. of 85% arsenic acid solution, the mixture is stirred until

precipitation is complete, and then kept at 0° for ten minutes. If at this point the mixture forms a hard mass, indicating an oil rich in cineole, 5 c.c. of light petroleum are added. The mixture is then pressed between filter paper until the cineole arsenate is dry and separates readily when touched; the pressing is not complete while the mass remains hard. The cineole arsenate is now decomposed by heating it with water in a flask provided with a graduated neck, and the volume of the cineole is read. In the case of eucalyptus oils containing less than 25% of cineole, the separation of cineole arsenate is not quantitative, and it is necessary to add 5 c.c. of pure cineole to the 5 c.c. of oil taken for the estimation. The results obtained by the method are concordant within 2%.

W. P. S.

Estimation of Non-protein Nitrogen and Urea-nitrogen in Blood. C. G. L. Wolf (*J. Physiol.*, 1914, **49**, 89—94).—Modifications of the methods at present in use (Folin's, van Slyke's, etc.) are described; the apparatus used is figured. A considerable proportion of the residual nitrogen is not in a form which yields nitrogen with nitrous acid. W. D. H.

Estimation of Allantoin in Urine in the Presence of Dextrose. Robert Henry Aders Plimmer and Ruth Filby Skelton (*Biochem. J*, 1914, **8**, 641—648).—The estimation of allantoin in urine containing dextrose can be effected by Folin's magnesium chloride method if the sugar is first removed. This can be done by precipitation with basic lead acetate and sodium hydroxide if the proportions are $2C_6H_{12}O_6 : 5[Pb(OH)_2,PbAc_2] : 10NaOH$.

W. D. H.

Characteristic Reactions of Phenylalanine. L. Chelle (*Ann. Chim. anal.*, 1914, **19**, 109; from *Bull. Soc. Pharm. Bordeaux*, 1913).—An orange coloration is obtained when a solution of phenylalanine in concentrated sulphuric acid is treated with a drop of formaldehyde solution; the colour changes rapidly to brown. When a solution of phenylalanine in sulphuric acid is mixed with a drop of a solution of paracetaldehyde in 90% alcohol, a lemon-yellow coloration develops within about ten minutes; this coloration increases gradually in intensity, and, after one hour, exhibits a green fluorescence. The reaction with paracetaldehyde may be used for the colorimetric estimation of phenylalanine. W. P. S

Detection of Cocaine. G. Denigès (*Bull. Soc. Pharm. Bordeaux*, **52**, 385; from *Zeitsch. anal. Chem.*, 1914, **53**, 407).—If a 0·5% solution of a cocaine salt is treated with an equal volume of a 5% solution of sodium perchlorate, a precipitate composed of long, very fine needles is formed; with very small quantities, the precipitation is observed under the microscope.

New Test for Morphine. T. H. Oliver (*Chem. and Druggist*, 1914, **85**, 45; from *The Med. Chronicle*).—If a morphine solution

is treated with a few c.c. of hydrogen peroxide and a small quantity of concentrated ammonia, and then stirred with a piece of copper wire, the previously colourless solution assumes a deep port-wine tint; there is also a considerable evolution of gas. The test is stated to be capable of detecting as little as 0·02 mg. of morphine, but in dealing with very small amounts, a few drops of potassium cyanide solution should be added before the copper wire is introduced. Conversely, the reaction is also a sensitive test for copper. Methylamine may be substituted for the ammonia in the test, but not dimethylamine or sodium hydroxide. Codeine and dionine (methyl- and ethyl-morphine respectively), which cannot be distinguished from morphine by the usual tests, do not give the reaction; *apo*morphine yields an orange coloration, but negative results are obtained with strychnine, brucine, atropine, narcotine, heroine, cocaine, nicotine, cephaeline, emetine, veratrine, physostigmine, pilocarpine, and coniine. W. P. S.

Detection of Oxymorphine in the Presence of Morphine. L. GRIMBERT and A. LECLÈRE (*J. Pharm. Chim.*, 1914, [vii], **10**, 425—428).—When a solution containing oxymorphine hydrochloride is treated with two drops of 1% potassium ferricyanide solution and two drops of sodium acetate solution, a turbidity or precipitate is produced; this test will detect the presence of 1 part of oxymorphine in 20,000 parts of solution, and the reaction is not given by morphine, codeine, thebaine, *apo*morphine, quinine, strychnine, brucine, atropine, or caffeine. If the precipitate is collected, dissolved in hydrochloric acid, and the solution neutralised with sodium carbonate, the precipitate is formed again, but dissolves in an excess of sodium carbonate; an excess of potassium hydrogen carbonate does not, however, dissolve the precipitate. Pure oxymorphine yields a red coloration when treated with sulphuric acid and formaldehyde; the addition of a trace of potassium ferricyanide changes the colour to bright green. The violet coloration obtained when morphine is treated with sulphuric acid and formaldehyde is not affected by the presence of potassium ferricyanide. W. P. S.

Quantitative Extraction of Diastases from Plant Tissues. R. W. THATCHER and GEO. P. KOCH (*J. Amer. Chem. Soc.*, 1914, **36**, 2542—2543).—A reply to Hulton's criticisms (*Analyst*, 1914, **39**, 260) of the authors' paper (A., 1914, ii, 508). E. G.

General and Physical Chemistry.

The Spectra of Helium and Hydrogen. E. J. Evans (*Phil. Mag.*, 1915, [vi], **29**, 284—297).—In view of the difficulty which attaches to the differentiation of the series lines of hydrogen and helium, experiments have been made to obtain the helium spectrum free from hydrogen lines, and also to obtain more accurate values for the wave-lengths of the lines of the Pickering series. The results show that with a helium discharge tube, which shows no trace of the hydrogen lines of the Balmer series, it is possible to observe the first member (λ 4686) of the series $\nu = 109750\ [1/(1\frac{1}{2})^2 - 1/(n/2)^2]$, and also a line ($\lambda$ 6560·4) which agrees in wave-length with the first member of the series $\nu = 109750\ [1/2^2 - 1/(n/2)^2]$, which includes the Pickering lines and the helium lines predicted by Bohr on the basis of his theory of the constitution of the helium atom.

The wave-lengths of the Pickering lines agree with the values calculated by Bohr within the limits of experimental error.

The results point to the conclusion that the series spectrum of hydrogen consists only of lines which are represented by the formula $\nu = 109704\ (1/n_1^2 - 1/n_2^2)$, and that the series spectrum of helium consists, in addition to the ordinary helium lines, of all the lines which are represented by the formula $\nu = 109750\ [1/(n_1/2)^2 - 1/(n_2/2]^2$. H. M. D.

Light Absorption and Fluorescence. II. E. C. C. Baly (*Phil. Mag.*, 1915, [vi], **29**, 223—240. Compare A., 1914, ii, 318).—As a consequence of the application of the quantum theory to the phenomena of light absorption and fluorescence, the author has been led to the conclusion that, if ν_x is the frequency of the characteristic infra-red vibration, energy can only be absorbed at the frequencies ν_1, ν_2, ν_3, etc., where ν_1, ν_2, ν_3 are successive multiples of ν_x. It follows that the absorption bands must show a constant frequency difference.

Assuming that the bands in the short-wave infra-red region are due to atomic vibrations, and those in the ultra-violet are due to electronic vibrations, it should be possible to combine these two vibrations in the manner indicated by Bjerrum (A., 1912, ii, 1114). If then ν is the characteristic vibration frequency in the ultra-violet, we should expect to find pairs of absorption lines with frequencies equal to $\nu \pm \nu_x$, where ν_x represents the frequencies of the short-wave infra-red bands. The same relationship is, of course, to be expected in the case of the fluorescence bands.

The structure of the ultra-violet absorption spectrum of benzene is cited as evidence in support of the correctness of the above views. It is found that the lines form a series of pairs which are symmetrically distributed about a central line, and that every

infra-red band in the short-wave region has a corresponding line or pair of lines in the ultra-violet absorption spectrum.

The spectra of toluene, *o*-, *m*-, and *p*-xylenes and naphthalene have also been examined from this point of view. On account of the lack of symmetry of the molecule, it cannot be expected that the absorption of these substances should exhibit the same degree of symmetry as is found with benzene. Of the disubstituted derivatives, the para-isomeride is the most symmetrical, and this is also found to be expressed in the structure of the ultra-violet absorption spectrum. In toluene, *o*-xylene, and *m*-xylene the want of molecular symmetry finds expression in the existence of fewer absorption lines on the ultra-violet side of the central line. H. M. D.

The Phototropy of Inorganic Systems. System of Strontium Sulphide. José Rodriguez Mourelo (*Compt. rend.*, 1915, **160**, 174—176. Compare A., 1914, ii, 159).—A study of the phototropy and phosphorescence of strontium sulphide when mixed with one or two phosphorogens. The experimental results are given for mixtures of strontium sulphide with varying proportions of manganese alone or manganese and bismuth, the mixtures being prepared by adding to strontium carbonate, 0·15% of anhydrous sodium carbonate, 0·05% of sodium chloride, the given amount of the phosphorogen, and lastly flowers of sulphur, and maintaining the whole mass at a red heat for four hours. The theoretical discussion of the results is reserved for a later paper. W. G.

Optical Superposition. IV. *l*-Menthylamine Tartrates and *l*-Amyl Dimethoxysuccinates. Thomas Stewart Patterson and Dorothy Christina Patterson (T., 1915, **107**, 142—155. Compare T., 1907, **91**, 705).—Unsound methods of testing the validity of van't Hoff's principle of optical superposition have been adopted by Walden and Guye. Tschugaev and Glebko, employing a more trustworthy method, draw the conclusion that their results agree with the demands of the principle, at least as a first approximation (A., 1913, ii, 897); they have, however, overlooked the really important question, which is, whether the difference between the mean of the rotations of the *d*-*A*, *d*-*B* and *d*-*A*, *l*-*B* compounds and that of the *d*-*A*, *i*-*B* compound is greater or less than the experimental error. If it is greater, van't Hoff's principle is disproved, but the converse is not necessarily true.

The authors have examined the three di-*l*-menthylamine tartrates and the three di-*l*-amyl dimethoxysuccinates. In the case of the former in methyl-alcoholic solution ($c=1·311$), $[M]_D^{22}$ has the value $-193·2°$ for *l*-menthylamine *l*-tartrate, $-57·9°$ for *l*-menthylamine *d*-tartrate (mean, $-125·5°$), and $-147·5°$ for *l*-menthylamine *i*-tartrate. Similar results are obtained for the three di-*l*-amyl dimethoxysuccinates at 20°, 60°, 100°, and 140°, but the results contain an element of uncertainty since the *l*-amyl alcohol used in the investigation was not quite pure. The rotation of dimethyl *d*-dimethoxysuccinate has been examined from about $-20°$ to 180°, in the homogeneous condition, and also in solution in ethylene dibromide and in nitrobenzene.

Alkyloxy-esters are readily obtained; for example, dimethyl dimethoxysuccinate is prepared almost quantitatively by the gradual addition of silver tartrate to silver oxide and boiling methyl iodide. C. S.

Special Case of Racemism. M. Padoa and G. Rotondi (*Gazzetta*, 1915, **45**, i, 51—56).—In his theoretical considerations dealing with the means of distinguishing racemic compounds, mixed crystals, and inactive conglomerates, Roozeboom (A., 1899, ii, 401) did not take into account cases of polymorphism with labile modifications, which Tammann's investigations have shown to be very common. In order to ascertain what influence such complications exert on the characterisation of inactive mixtures, the authors have investigated the case of bromocamphor, each enantiomorph of which crystallises in two forms: one labile with m. p. 45° difficult to observe, and the other stable, m. p. 75°. Determination of the labile and stable solidifying points of various mixtures of *d*- and *l*-bromocamphor shows that, at a definite concentration, the stable form becomes labile and vice versa. The form of the solidification curves and the composition of the different solid phases which separate indicate that the racemic compound exists between 44° and 50·5°, but that it is resolved at lower temperatures into inactive agglomerates T. H. P.

Temperature Coefficients of Phototropic Transformations. M. Padoa and G. Tabellini (*Gazzetta*. 1915, **45**, 10—15).—Preliminary experiments with piperil-*o*-tolylosazone and benzaldehyde-phenylhydrazone show that the thermal coefficients of the decolorisation of these compounds in the dark are comparable in magnitude with those of ordinary reactions occurring without the aid of light, whilst the influence of the temperature on the darkening of the same compounds in the light is very slight. The conclusion is drawn that phototropic transformations exhibit the characters of true chemical reactions. T. H. P.

The Magnetic Deflexion of the Recoil Stream from Radium-*A*. H. P. Walmsley and W. Makower (*Phil. Mag.*, 1915, [vi], **29**, 253—258. Compare Abstr., 1910, ii, 1022 and 1023).—If the velocity of the recoil particle is in agreement with the simple application of the law of momentum, the radius of curvature of the particle in a magnetic field should be twice that of the α-particle simultaneously expelled, since the recoil particles carry one atomic charge and the α-particle carries two. Measurement of these radii of curvature in the same magnetic field for the α-particles of radium-*A* and the recoil particles of radium-*B* were made in a vacuum by means of a photographic plate. It was found that if the plate were left for three hours after receiving the recoil particles the α-rays from the radium-*C* formed in the interval produced a measurable image. As a mean of five experiments the 2:1 ratio in the radii of curvature was found to hold with considerable accuracy. F. S.

The Velocity of the α-Particles from Radium-*A*. N. TUNSTALL and W. MAKOWER (*Phil. Mag.*, 1915, [vi], **29**, 259—260. Compare preceding abstract).—With the apparatus used to measure the magnetic deflexion of the recoil particle from radium-*A*, lines on the plate due to the α-particles of radium-*C*, formed during the exposure from radium-*A*, were observed in addition to those from the α-particles of radium-*A*. A direct comparison of their radii of curvature gave the ratio 0·8792. Taking the velocity of the α-particles of radium-*C* as $1{\cdot}922 \times 10^9$ cm. per sec., that of the α-particles of radium-*A* is $1{\cdot}690 \times 10^9$, in good agreement with the value $1{\cdot}693 \times 10^9$ calculated indirectly from the ranges of the two α-particles by Geiger's formula. F. S.

Interaction of Hydrogen and Chlorine under the Influence of α-Particles. HUGH STOTT TAYLOR (*J. Amer. Chem. Soc.*, 1915, **37**, 24—38).—Lind (A., 1912, ii, 513, 1027) studied the ozonisation of oxygen under the influence of α-particles, and formulated an ionic theory of ozonisation which was shown to be applicable to all the reactions caused by radioactive energy with the exception of the combination of hydrogen and chlorine. An investigation of the combination of hydrogen and chlorine under the influence of the α-particles from radium emanation has therefore been carried out by the method used by Lind in his work on ozonisation.

The results show that the union of hydrogen and chlorine under the influence of α-particles is a reaction of the first order. The hydrogen chloride formed does not affect the velocity. Oxygen retards the reaction, the velocity at all stages of the decomposition being inversely proportional to the oxygen concentration. The experimental facts may be interpreted by the reaction velocity equation $d[2HCl]/dt = k \cdot J[Cl_2]/[O_2]$, where J is the radiant energy employed. It is evident, therefore, that the reaction is strictly analogous to the photochemical reaction. The bearing of the results on the problem of the photochemical and Röntgen-ray reactions is discussed. E. G.

Electric Conductivity of Mixtures of Oxygen and Autoxidising Vapours of Benzaldehyde and Pinene. W. P. JORISSEN and J. A. VOLLGRAFF (*Chem. Weekblad*, 1915, **12**, 93—97).—Under the influence of the rays of a uviol lamp the autoxidation of benzaldehyde or pinene increases the electric conductivity of oxygen. A. J. W.

Electrical Conductivity of Solutions of Certain Electrolytes in Organic Solvents. J. N. PEARCE (*J. Physical Chem.*, 1915, **19**, 14—49).—Measurements have been made of the electrical conductivity of various electrolytes dissolved in aniline, quinoline, and pyridine at 0°, 25°, and 35° or 50°. The salts examined in aniline solution were silver nitrate, aniline hydrochloride and hydrobromide, ethylaniline hydrochloride, mercuric iodide, ammonium thiocyanate, and tetraethylammonium iodide; in quinoline solution, aniline hydrobromide, silver nitrate, and cobalt chloride; in pyri-

dine solution, silver nitrate, lithium chloride, bromide and iodide, sodium iodide, potassium and ammonium thiocyanates, mercuric chloride, bromide, and iodide, cupric chloride and nitrate, cobalt chloride and cadmium nitrate. Tables are given showing the variation of the molecular conductivity with the dilution at different temperatures, and also the magnitude of the temperature-coefficient. The data afford examples of solutions in which the molecular conductivity increases with the concentration, and also of solutions for which the molecular conductivity attains a minimum at a particular concentration. An attempt is made to explain the behaviour of such solutions by the formation of polymerised molecules which readily undergo ionisation. The ions in the more concentrated solutions differ, therefore, from those which are formed in more dilute solutions. H. M. D.

Inclusion of Electrolyte by the Deposit in the Silver Voltameter. T. W. RICHARDS and F. O. ANDEREGG (*J. Amer. Chem. Soc.*, 1915, **37**, 7—23).—An account is given of an investigation of the presence of included electrolyte in the crystalline silver deposited in a silver voltameter (or coulometer). The porous cup coulometer (Richards and Heimrod, A., 1902, ii, 592) was employed.

The presence of included electrolyte was proved (1) by the quantitative analysis of the crystals dried at 160°, (2) by igniting the crystals on the cathode at a dull red heat, (3) by igniting the crystals removed from the cathode in a quartz tube so arranged as to prevent evaporation of silver, and (4) by showing that simultaneous deposits which were of unequal weight before ignition had become equal after ignition.

The included mother liquor has been shown to be partly within the crystals and partly between the crystals and the wall of the cathode. The amount of the included impurity is approximately proportional to the area of the surface on which the silver is deposited, and increases with the roughness of the cathode; it was found to vary from 0·004 to 0·035% of the weight of the silver. The silver left after ignition at a dull red heat contains less than 0·001% of impurity.

Bates and Vinal (A., 1914, ii, 520), in comparing the iodine coulometer with the silver coulometer, obtained a value, 126·898, for the atomic weight of iodine when that of silver was taken as 107·88; when corrected for inclusions in the silver, this becomes 126·917, which agrees much more closely with the best result, 126·932, obtained by Baxter (A., 1911, ii, 112).

It is pointed out that the correction for included electrolyte is of great importance, since it affects the value of the electrochemical equivalent, the Faraday, the value assigned to the Weston cell, and all ratios of atomic weights determined electrically. E. G.

Behaviour of Half-Watt Lamps Filled with Nitrogen Containing a Small Proportion of Methane or Carbon Monoxide. L. HAMBURGER (*Chem. Weekblad*, 1915, **12**, 62—73).—The presence of more than 0·05% of methane, or 2% of carbon

monoxide, in the nitrogen employed for filling ½-watt lamps renders the filament brittle, and shortens the life of the lamp.

A. J. W.

New Thermochemical Method for Sub-dividing Accurately a Given Interval on the Thermometer Scale. THEODORE W. RICHARDS and THORBERGUR THORVALDSON (*J. Amer. Chem. Soc.* 1915, **37**, 81—86).—A method is described for accurately dividing any given interval on the thermometer scale by thermochemical experiments. As an example of the method, the heat of dilution of hydrochloric acid has been studied. It has been found that by choosing varying initial concentrations and varying final concentrations, temperature changes can be obtained of any magnitude from a few thousandths to several tenths of a degree. Acid of the strength $HCl,20H_2O$ was diluted with exactly $80H_2O$; this reaction gives sufficient heat to raise the temperature of the total amount of liquid about 0·25°, and by this means the interval between 16° and 20° was divided into sixteen parts. Allowance has to be made, of course, for the temperature-coefficient of the reaction and other details depending on changing heat capacity. The method is very suitable for standardising short ranges such as are used in thermochemistry.

E. G.

Thermal Dilatation of Sodium, Potassium, and Lithium. ARCIERO BERNINI and CARLO CANTONI (*Nuovo Cim.*, 1914, [vi], **8**, ii, 241—260).—By means of a dilatometer of special construction containing vaseline oil, the authors have measured the thermal expansions of these metals at a number of temperatures ranging from 0° to 235°. In all cases the expansions are expressible by equations of the second degree with reference to the temperature, the values of the coefficients, α and β, of t and t^2 respectively, being as follows:

		Temperature interval.	α.	β.	Increase of volume on fusion.	Melting point.
Na	Solid.....	0—78°	$0{\cdot}0_31816$	$0{\cdot}0_62280$	2·031%	97·6°
	Liquid ...	100—235°	$0{\cdot}0_32599$	$0{\cdot}0_62286$		
K	Solid.....	0—56°	$0{\cdot}0_32112$	$0{\cdot}0_6155$	2·44%	62·04°
	Liquid ...	78—235°	$0{\cdot}0_32681$	$0{\cdot}0_6210$		
Li	Solid.....	0—178°	$0{\cdot}0_31535$	$0{\cdot}0_792$	1·51%	180·1°
	Liquid ...	182—235°	$0{\cdot}0_31743$	$0{\cdot}0_6106$		

The low values obtained by Hackspill (A., 1913, ii, 503) for the increase in volume of sodium on fusion and for the melting point of this metal are attributed to the use of impure material.

T. H. P.

The Coefficient of Expansion. L. GAY (*Compt. rend.*, 1915, **160**, 64—67).—A mathematical paper in which the author shows that, in the case of a substance giving more than one hydrate, it is possible, starting with the coefficients of expansion of these hydrates, to calculate the expansion pressures corresponding with

equilibria between these hydrates taken two at a time. The limits of perfect stability, with respect to all these hydrates, of any one of them will be, on the one hand, the highest pressure amongst those corresponding with equilibrium mixtures with the lower hydrates, and, on the other, the lowest pressure amongst those corresponding with equilibrium mixtures with the higher hydrates. If this first limit pressure is greater than the second, then the hydrate will always be in a metastable state. W. G.

The Solubility of Hydrates. L. GAY (*Compt. rend.*, 1915, **160**, 171—173).—A mathematical paper in which the author shows that it is possible to calculate the limits of stability of a hydrate with respect to its solution from the coefficient of expansion of the hydrate with respect to the anhydrous compound (preceding abstract). W. G.

Specific Heat at Low Temperatures. I. Measurements of the Specific Heat of Lead between 14° and 80° and of Copper between 15° and 22° (absolute). W. H. KEESOM and H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 894—914).—The method employed was that developed by Nernst, in which a block of the metal, provided with wires for heating and temperature measurement, is suspended in a vacuum in a liquid hydrogen thermostat. A measured quantity of heat is developed within the block by an electric current, and the increase of temperature produced is determined. A gold wire resistance thermometer was used for this purpose, this being calibrated with the aid of a hydrogen vapour-pressure apparatus, and by this means the scale of the gold resistance thermometer could be reduced to that of platinum. A constantin wire was employed for the heating current, and this was calibrated in the same manner as the resistance thermometer.

The results obtained with lead show that the atomic heat C_p has the value 1·56 at 14·19°, 2·98 at 22·31°, 5·04 at 46·25°, and 5·67 at 80·86°. Over this range, the variation of the heat capacity agrees fairly well with Debye's formula, although the deviations exceed the uncertainty of the experimental results in the region of liquid hydrogen temperatures.

For copper, the atomic heat C_p increases from 0·0500 at 15·24° to 0·1414 at 21·505°. Over this range of temperature, the atomic heat agrees with that calculated from Debye's formula within 2%. H. M. D.

Metastability of the Metals in Consequence of Allotropy and its Significance for Chemistry, Physics, and Technics. III. ERNST COHEN and G. DE BRUIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 926—934. Compare A, 1914, ii, 799).—Reference is made to the different values which have been obtained for the specific heat of certain metals at one and the same temperature by different observers. These differences are supposed to be

partly the result of differences in the previous thermal history of the metals.

The recent measurements of Griffiths (A., 1914, ii, 245; compare also A., 1914, ii, 798) of the specific heat of sodium in the solid and liquid states show clearly that the true specific heat of solid sodium is dependent on its previous thermal history. The slowly cooled and the quenched metals yield definite and reproducible values of the specific heat at a definite temperature. An intermediate previous thermal treatment gives values for the specific heat which fall between the values obtained for the annealed and the chilled metal respectively.

These observations lead the authors to the conclusion that sodium is enantiotropic, and that a transition temperature will be found between 0° and 90°. As usually obtained, sodium represents a metastable system, consisting of a mixture of two allotropic modifications the proportions of which depend on the previous thermal treatment. H. M. D.

Measurement of Vapour Pressure Lowering by the Air Saturation Method. EDWARD W. WASHBURN and EDWARD O. HEUSE (*J. Amer. Chem. Soc.*, 1915, **37**, 309—321).—This work was undertaken with a view to obtaining an accurate method for investigating the molecular constitution of aqueous solutions over a large range of concentrations and at a constant temperature.

A modification of the air saturator method is described which combines the differential process first used by Ostwald and Walker with the absorption of the moisture in absorbers of such size and form as to be capable of being accurately weighed. The type of absorber and the comparatively high rate of aspiration used necessitated the employment of small differential manometers to measure the fall in pressure through the apparatus. In order to test the trustworthiness of the method, measurements have been made with weight molar solutions of sucrose at 25°. The average deviation of the individual results from the mean was 0·4%, whence it is evident that fairly concordant results can be obtained at this concentration. The accuracy of the results was tested by calculating the corresponding values of the osmotic pressure and comparing them with the values obtained by Morse by direct measurement; the agreement between these values shows that the air-saturation method gives correct results.

The work has shown that by means of the authors' apparatus values of $(p_0-p)/p_0$ of the order of magnitude of 0·02 can be measured with an accuracy of 0·5% in an experiment of twenty-four hours' duration. The method is now being extended to the measurement of the lowering of vapour-pressure of solutions of mannitol at 25° and 35°. E. G.

Fractional Distillation with Regulated Still-heads. I. Cases in which the Boiling Point Passes through a Maximum or a Minimum. M. A. ROSANOFF and C. W BACON (*J. Amer. Chem. Soc.*, 1915, **37**, 301—309).—The first systematic investigation of a

regulated still-head was carried out by Brown (T., 1880, **37**, 49; 1881, **39**, 517), who made extensive observations on the effect of cooling a saturated binary vapour to a given constant temperature, and enunciated the following law: "In distillation with a still-head maintained at a constant temperature the composition of the distillate is constant, and is identical with that of the vapour evolved by a mixture whose boiling point equals the temperature of the still-head."

Further investigation of the regulated still-head has shown that this law requires serious modification before it can serve as the basis of a rational process of fractional distillation. In the present paper the authors show how the regulated still-head should be expected to function in cases in which the boiling-point curve passes through a maximum or minimum, and in which, therefore, there may be two mixtures boiling at one and the same temperature, or, in the words of Brown's law, two mixtures "whose b. p. equals the temperature of the still-head."

Experiments have been made with mixtures of carbon disulphide and acetone, and of ethyl iodide and ethyl acetate, in which the boiling-point curve passes through a minimum, and with mixtures of chloroform and acetone in which the boiling-point curve passes through a maximum. In the case of the experiments with carbon disulphide and acetone, the temperature of the still-head was maintained at 40°; a mixture containing only a small percentage of acetone yielded seven consecutive fractions containing 75·1—75·2 molar % of carbon disulphide, whilst a mixture containing only 29% of carbon disulphide gave fifteen consecutive fractions containing 55·2—55·4 molar % of carbon disulphide. The temperature of the still-head was kept at 71·22° during the experiments with ethyl iodide and ethyl acetate; a mixture containing only a small percentage of ethyl acetate gave four consecutive fractions containing 89·9, 89·3, 89·2, and 89·1 molar % of ethyl iodide respectively, whilst a mixture of the two components in about equal parts gave four consecutive fractions containing 49·4, 49·3, 48·9, and 48·9 molar % of ethyl iodide. In the case of the experiments with chloroform and acetone, the still-head was maintained at 62°; a mixture containing about 6% of acetone gave six consecutive fractions containing 92·3—92·5 molar % of chloroform, whilst a mixture containing rather more than 40% of chloroform yielded six consecutive fractions containing 30·8—30·9 molar % of chloroform. E. G.

Improved Heating Apparatus for Maintaining Constant Temperatures in Work with Polarimeters and Refractometers. J. N. Pearce (*J. Amer. Chem. Soc.*, 1915, **37**, 147—149).—The apparatus consists of a cylindrical vessel surrounded by a layer of felt or asbestos paper. On the bottom of this vessel is fixed a small cylinder, within which rotates a motor-driven stirrer. At a point a little below the water-level is an iron tube, and a similar tube opens directly into the small cylinder at the bottom of the bath. The open ends of these tubes are attached directly to a

jacketed observation tube by pieces of rubber tubing. The water is heated by one or two immersed incandescent lamps, and the temperature is electrically controlled by a contact toluene regulator in series with a telegraph relay and battery. By heating the bath with a Bunsen burner, the water can be rapidly heated and adjusted to any higher temperature than that obtainable from the lamps. The bath is equally adapted for use with ice; for temperatures between 0° and that of the room, a cooling coil connected with the water supply may be introduced. The temperature of the bath can be maintained constant within 0·01—0·02° for any desired length of time. E. G.

Densities and Degrees of Dissociation of the Saturated Vapours of the Ammonium Haloids and the Related Thermal Data. ALEXANDER SMITH and ROBERT H. LOMBARD (*J. Amer. Chem. Soc.*, 1915, **37**, 38—70).—Previous determinations of the vapour densities of the ammonium haloids have been made on the assumption that the dissociation is complete. This assumption, however, is far from correct, and only the densities of the unsaturated vapours have been measured. An investigation has now been made of the saturated vapours by the method employed by Smith and Menzies (A., 1912, ii, 114) for determining the density of saturated mercurous chloride vapour. The results, together with the corresponding dissociation pressures (Smith and Calvert, A., 1914, ii, 628), have rendered possible the calculation of the values of the degrees of dissociation, the dissociation constants, the partial pressures of the dissociation products, the heats of dissociation, and the latent heats of vaporisation.

Ammonium chloride vapour is dissociated between 280° and 330° to the extent of 67—63%, the degree of dissociation decreasing slightly between these temperatures. Ammonium bromide vapour is dissociated to about 39% at 320°, and at higher temperatures the percentage dissociation decreases linearly, reaching about 10% at 388°. Ammonium iodide vapour is associated, especially at lower temperatures, but as the temperature rises the amount of association decreases. The assumption that ammonium haloid vapours are completely dissociated is therefore no longer tenable.

The dissociation constant of ammonium chloride vapour increases steadily with the temperature, whilst that of ammonium bromide vapour reaches a maximum at about 320°, and then decreases.

The heat of dissociation of ammonium chloride vapour, computed by the van't Hoff equation, is represented by the relation U(the heat evolved) $= -12800 - 0{\cdot}00967T^2$ cal. The dissociation of ammonium bromide vapour above 320° is accompanied by the development of heat, but the actual value of the heat of dissociation cannot be computed.

The latent heats of vaporisation were calculated by the Clausius-Clapeyron equation. That of ammonium chloride is 32·9 Cal. between 280° and 330°, and is constant within 1%; that of ammonium bromide is 28·7 Cal. at 320°, and decreases to 24·1 at

388°; that of ammonium iodide increases from 18·0 Cal. at 300° to 24·2 at 380°. E. G.

Molecular Association of Liquids. DANIEL TYRER (*J. Physical Chem.*, 1915, **19**, 81—112. Compare A., 1912, ii, 739).—A further examination of the methods which have been suggested as suitable for the determination of the degree of association of a liquid. In addition to the conditions laid down in the previous paper (*loc. cit.*), it is now shown that any equation which can be used for the accurate determination of association factors must be valid for mixtures as well as for pure liquids. This is necessitated by the fact that an associated liquid is, in general, a mixture of different kinds of molecules.

Approximate minimum values of the association factors at the boiling points may be obtained by means of the empirical equation $T_s = K\sqrt[3]{V_s}\log M$, in which T_s is the boiling point, V_s the molecular volume at the boiling point, M the molecular weight, and K a constant equal to about 37. The minimum values thus obtained are: water, 6·3; methyl alcohol, 2·55; ethyl alcohol, 1·89; formic acid, 2·71; acetic acid, 2·05.

The relation of Kistiakowski, $\alpha^2 M/T_s = K$, where α^2 is the capillary rise in a tube of 1 mm. radius and K is a general constant, may also be considered a good test for association.

Molecular weights of liquid substances may also be calculated from the equation $M(C_p - C_v)/V^{\frac{1}{3}} = K$, in which C_p and C_v are the specific heats at constant pressure and constant volume, and V is the molecular volume. This equation is approximately satisfied by the data for a considerable number of normal liquids, but others, usually regarded as normal, would appear to be associated on the basis of this equation. This is the case, for example, with carbon disulphide, and it is shown that this substance behaves frequently as if it were an associated liquid, although several of the recognised methods of molecular-weight measurement indicate that it consists essentially of simple molecules.

It has been shown previously (A., 1914, ii, 431) that the equation $\beta\gamma^{4/3}/T^{1/3} = K$, in which β is the isothermal compressibility, γ the surface tension, and T the absolute temperature, holds for a large number of liquids. This relation does not involve the molecular weight, but water, ethyl alcohol, and carbon disulphide yield values for K which are too high. To explain these and other anomalies, it is suggested that the mean kinetic energy of the molecules of such liquids is less than the kinetic energy of free gas molecules at the same temperature. In the case of carbon disulphide, this is the only factor which produces anomalies in certain of the physical properties, whilst with water and the alcohols molecular association also comes into play. H. M. D.

Capillarimeter, Viscostagonometer, and Stalagmometer. I. TRAUBE and R. SOMOGYI (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 485—490).—These three apparatuses give practically identical results for the surface tension of non-colloidal liquids. With

colloidal liquids, the results obtained with the viscostagonometer are lower than those given by the stalagmometer, because the colloidal material slowly moves towards the surface. The viscostagonometer measures the surface tension of the older (longer existing) surfaces, whereas the stalagmometer measures those newly formed. The capillarimeter cannot be used with colloidal liquids. H. W. B.

Stalagmometric Studies of Solutions of Colloids and Crystalloids. IV. Diffusion in the Surface Layer. L. Berceller (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 124—132. Compare A., 1913, ii, 760).—In the measurement of the surface tension of solutions by means of Traube's stalagmometer, varying results are obtained, with varying rates of formation of the drops. The quicker the drops form and fall, the greater the value obtained for the surface tension. The interpretation given to this phenomenon is that the surface layer forms so rapidly in the drop that the dissolved substance has not sufficient time to accumulate in it and attain to the concentration it reaches when the surface of the liquid is at rest. It follows that the slower the rate of diffusion of a substance, the more marked should be the alteration of the surface tension of its solution with change in the rate of drop formation, and in accord with this it is found that solutions of colloids, such as the proteins and soaps, produce much greater variations than solutions of the crystalloids, such as acetone and the alcohols. H. W. B.

Diffusion of Hydrogen through Palladium. Alfred Holt (*Proc. Roy. Soc.*, 1915, [*A*], **91**, 148—155).—The diffusion of hydrogen through a palladium septum at temperatures ranging from 70° to 300° has been investigated by (1) measurements of the rate of diffusion of hydrogen at constant pressure into a vacuum; (2) measurements of the rate of diminution of pressure when diffusion takes place into a vacuum; (3) measurements of the rate of diminution of pressure on one side and increase of pressure on the opposite side of the septum during the diffusion of a definite quantity of hydrogen.

If the logarithm of the pressure (decreasing) is plotted against time, the experimental data for each experiment in which the pressure decreases, yield two intersecting straight lines. In the case of increasing pressures, the graph of $\log(760 - p)$ against time affords similarly two straight lines. The conclusion drawn from the results is that at pressures between 700 and 100 mm. the rate of diffusion is proportional to the pressure of the hydrogen. As in the case of the rate of dissolution of hydrogen in palladium, where discontinuity has also been observed, the two straight lines of different slope are accounted for by metallic allotropes.

At pressures below 100 mm., the diffusion becomes much slower, and the rate of diffusion does not seem to be related to the pressure in any simple manner. H. M. D.

Effect on their Solution Tensions of Dissolving the Alkali and Alkali Earth Metals in Mercury, and the Constitution of Such Solutions. GEORGE MCPHAIL SMITH (*J. Amer. Chem. Soc.*, 1915, **37**, 76—80).—In an earlier paper (A., 1908, ii, 159) it was suggested that, in some cases, when metals are dissolved in mercury, compounds of mercury and the dissolved metal are formed containing a single atom of the latter in the molecule. More recently (A., 1914, ii, 543) the author has shown by means of the diffusion method that in mercury solution compounds probably exist, such as $LiHg_3$, $NaHg_5$, KHg_6, $CaHg_5$, and $BaHg_6$.

Confirmatory evidence has now been obtained by a study of the solution tensions of the alkali and alkali earth metals in mercury. If small, equimolar quantities of these metals in equal, large quantities of mercury exist in solution in the form of free monatomic molecules, their solution tensions should be lowered, but in a more or less uniform manner; the relative magnitude of the solution tensions should not be greatly altered. If, however, the metals combine with mercury to form compounds containing only one atom of the amalgamated metal to the molecule, the solution tensions should be lowered to a much greater degree, and not uniformly, but in accordance with the relative affinities of the metals for mercury. The results of the present work show conclusively that the latter actually occurs; the solution tensions of the metals when dissolved in excess of mercury decrease in the order K, Rb, Cs, Na, and Ca, Sr, Ba. E. G.

Electric Synthesis of Colloids. JNANENDRANATH MUKHOPÂDHYÂYA (*J. Amer. Chem. Soc.*, 1915, **37**, 292—297).—This investigation was undertaken in order to elucidate the process of the formation of colloid solutions by Bredig's electric method (A., 1899, ii, 78). Benedicks (A., 1913, ii, 99, 307) has expressed the opinion that the process is mainly of a thermal character, the metal melting into fine drops, which remain suspended.

Experiments have now been made in which various substances were placed between the carbon electrodes of an electric arc immersed in water, and it has been found that at the intense heat of the arc discharge the substance is volatilised, and the fine particles on condensation form sols. The method gave good results with sulphur, selenium, and phosphorus; the sols were fairly stable, and showed the Tyndall phenomenon. In the case of cadmium and copper, the hot metal reacts with the water, with formation of some hydroxide; the colloidal solution obtained is unstable, and soon coagulates, the precipitate consisting of a mixture of the metal and its hydroxide. The method is very rapid in the case of mercury, and yields a stable grey sol. The results of these experiments support the view that the formation of the sols is a thermal process due to the high temperature of the electric arc. E. G.

Value of Viscosity Measurements for the Characterisation of Organic Colloids. J. SCHIBIG (*Intern. Zeitsch. phys.-chem. Biol.*

1914, **1**, 260—268).—A summary of the theoretical considerations already expressed in a published dissertation. H. W. B.

Study of the System: Water, Potassium Iodide, and Iodine at 0°. GRINNELL JONES and MINER LOUIS HARTMANN (*J. Amer. Chem. Soc.*, 1915, **37**, 241—258).—Bray and MacKay (A., 1910, ii, 820) have determined the conductivities at 25° of potassium iodide solutions saturated with iodine. A similar investigation has now been made at 0° by the same methods.

The conductivities of potassium iodide solutions and of the same solutions saturated with iodine have been measured at concentrations between 0·1*N* and 0·001*N*. The solubility of iodine in these potassium iodide solutions and in water has also been determined at 0°; the solubility in water is 0·0006383 mol. per litre. The viscosities of the solutions at 0° and 25° have been determined, and the results applied to the correction of the degree of dissociation of potassium iodide at these temperatures. The mobilities of the iodide and tri-iodide ions at 0° are 43·4 and 22·8 respectively. The hydrolysis constant of iodine in water at 0° is 9×10^{-15}.

Bray and MacKay found that at 25° the ratio of the iodide and tri-iodide ions, $I^-:I_3^-$, decreased from 1·14 to 0·99 with increasing concentrations of 0·001*N* to 0·1*N*, and became 0·35 at *N*. At 0°, however, no such marked deviation occurs, although a slight tendency in that direction appears in the 0·05*N*- and 0·1*N*-solutions. Assuming that this apparent deviation from the mass law at 25° is due to the formation of higher complexes than KI_3, it is evident that the formation of these higher complexes is much less at 0° than at 25°. E. G.

Equilibrium in the System: Water, Phenol, and Benzene. SHINKICHI HORIBA (*Mem. Coll. Sci. Kyoto*, 1914, **1**, 49—55).—The equilibrium relations in the above ternary system have been examined at 25°. The phenol in the solutions was estimated by means of bromine, and the benzene and water by measuring the quantities of each which were necessary for the production of permanent turbidity. The results are recorded in a series of tables, and also in the form of a triangular graph. H. M. D.

Theory of Dyeing. IV. WILDER D. BANCROFT (*J. Physical Chem.*, 1915, **19**, 50—64. Compare A., 1914, ii, 436).—A further discussion of observations recorded in the literature relating to the distribution of substances between solid and liquid phases. In general, these observations afford no evidence of the formation of definite compounds, and thus furnish support for the author's view that the formation of definite compounds plays no important part in the practice of dyeing. H. M. D.

Theory of Dyeing. V. WILDER D. BANCROFT (*J. Physical Chem.*, 1915, **19**, 145—158).—The question of the fastness of dyes is discussed by the methods followed in the previous papers belonging to this series (compare preceding abstract). It would appear that

the many contradictory statements relative to the fastness of dyes on different fibres are mainly due to unspecified differences in the conditions of the experiments. The fact that many dyes are faster to light in iron, chromium, and copper mordants, as compared with aluminium and tin mordants, is said to be probably due to differences in the absorption of light. H. M. D.

Rate of Reduction of Mercuric Chloride by Sodium Formate. G. A. LINHART (*J. Amer. Chem. Soc.*, 1915, **37**, 70—76).—In an earlier paper (A., 1913, ii, 490) an account was given of an investigation of the rate of reduction of mercuric chloride by phosphorous acid. A similar study has now been made of the reduction of mercuric chloride by sodium formate, with special reference to the influence of sodium chloride on it. This reaction has already been investigated by Findlay and Davies (T., 1913, **103**, 1550), who consider that it is of the second order, since when their results are substituted in an equation representing a reaction of the third order, the reaction velocity-coefficient gradually increases to about 40%, whilst if substituted in one of the second order the velocity-coefficient decreases by only about 17%. The present work shows that the mechanism of the reaction between mercuric chloride and sodium formate may be interpreted in a similar manner to that of mercuric chloride and phosphorous acid, and that concordant velocity constants may be obtained if the experiments are carried out under suitable conditions.

It has been proved, both experimentally and theoretically, that the reaction is one of the second order. The sodium chloride formed during the reaction exerts a remarkable retarding effect. This effect, however, was reduced to a minimum by using dilute solutions of mercuric chloride and by adding initially a large excess of sodium chloride to the reaction mixture, so that the amount of sodium chloride formed in the reaction was rendered negligible. Under these conditions, concordant velocity constants were obtained. E. G.

Oxidation of Sucrose by Potassium Permanganate. C. W. R. POWELL (*J. Roy. Soc. New South Wales*, 1914, **48**, 223—241).—Measurements have been made of the rate at which potassium permanganate reacts with sucrose in acid, neutral, and alkaline solution. The rate of the reaction is least in neutral solution, and higher oxides of manganese are precipitated during the course of the reaction unless a certain quantity of acid is present at the beginning. For this reason, the majority of the observations were made in acid solution.

The author considers that the results point to a bimolecular reaction, although the velocity-coefficient increases during the course of the change. The increase in velocity is attributed to the accelerating influence of the manganese sulphate which is formed during the reaction. Within certain limits the nature of the reaction does not seem to be affected by the concentration of the acid, but the initial velocity is approximately proportional to the

hydrogen-ion concentration. The velocity is increased in the ratio 3·0 : 1 for a rise of temperature of 10°.

Although dextrose reacts with permanganate more rapidly than sucrose, this does not seriously affect the results obtained, for the quantity of dextrose formed during the time required by the experiments is comparatively small. H. M. D.

Catalytic Action of Alkaloids on Various Physical and Chemical Processes (Precipitation, Oxidation, and Saponification). I. TRAUBE and N. ONODERA (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 148—157. Compare Traube, A., 1912, ii, 740).—An introductory paper giving results of experiments in which alkaloids have exerted an inhibitory or accelerating influence on the velocity of various reactions. Alkaloids, although univalent, greatly accelerate the precipitation of arsenious sulphide from its colloidal solution, and hasten the oxidation of oxalic acid by permanganate. A few alkaloids inhibit the saponification of ethyl acetate by potassium hydroxide, whilst the majority aid it. Pilocarpine and atropine have a similar action on the first two processes, but on the saponification process pilocarpine has a very strong accelerating, and atropine an inhibitory, action, so that in this case a striking example is afforded of the antagonistic action of these two alkaloids. The antagonistic action observed between these two drugs in the body in relation to gland secretion, dilation of pupil, etc., is possibly to be correlated with their action on hydrolytic processes.

H. W. B.

The Series Spectrum of Hydrogen and the Structure of the Atom. N. BOHR (*Phil. Mag.*, 1915, [vi], **29**, 332—335).—The author criticises certain deductions made by Allen (this vol., ii, 33), in which it was assumed that the nucleus of the Rutherford atom has the properties of a small magnet, in addition to its electric charge. The argument put forward shows that the suggestion of the nuclear magnet can scarcely be considered as supported by the accurate measurements made by Curtis (A., 1914, ii, 761) of the wave-lengths of the series lines in the hydrogen spectrum. In view of the doubling of the hydrogen lines, it seems unjustifiable to compare the results of these measurements with any theoretical formula. Since the distance between the components is much greater than the deviations from the Balmer formula, and since also the components are of unequal intensity, it is not possible to place any satisfactory interpretation on measurements of the "centre of gravity" of the lines. As a possible explanation of the doubling of the lines, it is suggested that this may be due to the orbits of the electron not being circular. H. M. D.

The Gyroscopic Theory of Atoms and Molecules. ALBERT C. CREHORE (*Phil. Mag.*, 1915, [vi], **29**, 310—332. Compare A., 1913, ii, 689).—A theoretical paper in which the author develops a theory of atomic structure which differs considerably from that of Ruther-

ford, according to which the electrons circulate in orbits which are very large compared with the radius of the central positive nucleus. In the author's theory the density of the positive and negative electricity is the same, and has a constant value which is approximately equal to 10^{12} grams per c.c. The mass of the atom is accounted for by the larger volume of the positive electricity, the ratio of the volumes of the positive and negative electricity being the ratio of the masses of the hydrogen atom and the electron.

It is assumed that there is no radiation of energy from the atom so long as the electrons describe circular orbits in the steady state, but a disturbance of this state may give rise to rapid nutations of the electrons, both natural and forced, which will account for the emission of *X*-rays. If there is more than one electron in the same orbit, the natural nutation frequencies are not easily obtained from analogy with gyroscopic equations, and it is assumed that these frequencies are proportional to the number of electrons per ring. This assumption, in combination with the grouping of the electrons which has been described previously (*loc. cit.*), leads to a tentative distribution of electrons which will account for the *K* and *L* series of *X*-ray spectra.

Light vibrations are attributed to the precessional frequencies of the electrons in their orbits, and it is shown that the principal constant in Balmer's formula for the hydrogen series can be expressed in terms of constants characteristic of the hydrogen molecule.

The atomic model described by the author is capable of response to any frequency of light, because there are precessional frequencies produced in the atom which are proportional to those of the impressed force. In this connexion it is pointed out that no form of atom, which is capable of resonance at fixed frequencies only, can account for the experimental facts relating to the photo-electric effect.

The theory shows further that there is a limiting value of the atomic weight in the neighbourhood of uranium. In this region the outside ring of electrons is unstable, and comparatively small forces suffice to drive an electron outside the region of positive electricity leading to an internal readjustment and the display of radioactive properties. H. M. D.

Calculation of the Molecular Dimensions from the Supposition of the Electric Nature of the Quasi-Elastic Atomic Forces. J. J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 877—884. Compare A., 1914, ii, 801).—A theoretical paper, in which the author makes use of a formula given by van der Waals in order to obtain values for the size of molecules. For argon, hydrogen, and helium the values obtained for the molecular diameter are 3·5, 3·2, and $3·2 \times 10^{-8}$ cm. respectively. In spite of the difference in molecular weight, there is therefore very little difference in the molecular diameter. For other, not too complex, substances the value obtained rarely exceeds 4×10^{-8} cm.

H. M. D.

Classification of the Elements. J. R. Rydberg (*J. Chim. Phys.*, 1914, **12**, 585—639).—A grouping of the elements is described, which differs in many respects from the Mendeléev system. The arrangement involves the view that the atomic weight is not a fundamental property of the elements, and hence it is not to be expected that the properties will be dependent on the atomic weight. The quantities which are substituted for the atomic weights, as being of fundamental character, are the successive integral numbers commencing with unity. The change of the independent variable is based on the idea that the "ordinal numbers" correspond with certain states which we designate as atoms, and which possess the property of mass. This property increases continuously as the corresponding ordinal N increases, although other properties show a more or less pronounced periodicity.

Arranged in the above manner, the elements fall into a series of groups containing $4p^2$ elements, where p is equal to 1, 2, 3, 4, . . . Thus the first group contains four elements, whilst the second, third, and fourth groups contain sixteen, thirty-six, and sixty-four respectively. Since the known elements terminate with uranium ($N=94$), the first four groups are more than sufficient to accommodate all the elements, and actually it is found that the elements belonging to the fourth group are confined to the first half of this group with the exception of radium (90), thorium (92), uranium (94), and three unknown elements (89), (91), and (93).

The first group, G_1, begins with hydrogen (1) and ends with helium (4), and between these are two more or less hypothetical elements supposed to be identical with coronium (2) and nebulium (3). The second group, G_2, begins with lithium (5) and ends with argon (20); the third, G_3, begins with potassium (21) and ends with xenon (56); whilst the incomplete fourth group, G_4, begins with cæsium (57) and includes all the remaining elements.

The first half of the fourth group terminates at niton (88), and from cæsium to niton there are 32 elements, whereas Mendeléev's system requires 36 elements in this interval. Plausible arguments are advanced in support of the smaller number which is required by the author's system of classification.

Although mechanical mass is an attribute which appears to be confined to the elements for which $N=$ or >1, it would seem that $N=0$ should correspond with a state of matter, and $N=0$ is supposed to represent the electron, which thus forms the first member of the entire series and the only member of the group G_0.

The author describes his methods by means of which it is possible to represent diagrammatically the relations between the groups and the periodic recurrence of atomic properties. In one of these, the members of the four groups are placed in order along successive turns of a spiral. Periodicity in properties is not only determined by a complete turn of the spiral, but recurrence of similarity in properties is also found in elements which occupy corresponding positions in the four quadrants of the successive turns of the spiral.

This periodicity is very clearly shown in respect of the valency and the valency relations exhibited by the author's system are discussed in detail. The analysis of the valency relations leads the author to the conclusion that the valency of an element is determined by the operation of two entirely different factors, one of which is independent of the ordinal number N, whilst the other is determined by the magnitude of N. When the first factor only operates, the probable valency is three, although the neighbouring valencies two and four may also be impressed upon the atom in certain cases. The relations exhibited by the valencies are considered to add considerable weight to the classification which the author describes. H. M. D.

Electron Conception of Valence. VI. Inorganic Compounds. J. M. Nelson and K. George Falk (*J. Amer. Chem. Soc.*, 1915, **37**, 274—286).—In this paper the electron conception of valence (A., 1911, ii, 104, 171; 1913, ii, 768; 1914, ii, 44, 193) is applied to the constitution and reactions of inorganic compounds, and particularly to the views of chemical structure based on the classifications developed by Werner. E. G.

Modified Kipp Generator. Theodore Cohen (*J. Amer. Chem. Soc.*, 1915, **37**, 145—146).—A simple form of gas generator is described, which can be used as a substitute for Kipp's apparatus, and is particularly suitable for the use of individual students for ensuring a ready supply of hydrogen sulphide.

It consists of three gas bottles, an inverted reservoir bottle for the acid, which is connected by rubber tubing to an upright bottle, which is in turn connected by a glass tube to another inverted bottle containing the ferrous sulphide or other material. The reservoir bottle is fitted with a thistle-funnel with bent-up tube for admitting the acid, and the generating bottle bears a glass tube which passes from the bottom of the bottle downwards through the stopper, is then bent outwards at right angles, and has a piece of rubber tubing and a pinch-cock at the end. On opening the pinch-cock the pressure within the apparatus is released, and acid flows down into the upright bottle, whence it is forced up into the generating bottle. On closing the pinch-cock, the acid is automatically driven back into the reservoir bottle. E. G.

Vacuum and Pressure Stopcocks. Merle Randall and F. Russell von Bichowsky (*J. Amer. Chem. Soc.*, 1915, **37**, 137—144).—A description is given of the form and dimensions of the various stopcocks used in the chemical laboratory of the University of California. These include different types of vacuum stopcocks, pressure stopcocks, and multiple stopcocks. E. G.

Inorganic Chemistry.

Molecular Weight of Sodium Carbonate and the Atomic Weight of Carbon Referred to Silver and Bromine. THEODORE W. RICHARDS and CHARLES R. HOOVER (*J. Amer. Chem. Soc.*, 1915, **37**, 95—107).—The molecular weight of sodium carbonate has been determined by the following method. A weighed amount of pure, fused sodium carbonate was dissolved in water and neutralised exactly with hydrobromic acid. The quantity of silver required to precipitate this hydrobromic acid was then determined by the usual process. The chemical equivalence between the weights of sodium carbonate and silver could thus be simply determined, and the silver haloid standard referred directly to sodium carbonate. A full account is given of the various precautions taken to ensure the purity of the materials and to eliminate all sources of error.

It has been found that 29·43501 grams of sodium carbonate are equivalent to 59·91676 grams of silver, and also to a weight of dilute hydrobromic acid capable of precipitating 104·3023 grams of silver bromide. From the results, the molecular weight of sodium carbonate and the atomic weight of carbon have been calculated, and found to be 105·995 and 12·005 respectively (Ag = 107·880; Br = 79·916; Na = 22·995). If the atomic weight of silver is taken as 107·871, and that of sodium 22·993, the atomic weight of carbon becomes 12·000. E. G.

Molecular Weight of Sodium Sulphate and the Atomic Weight of Sulphur. THEODORE WILLIAM RICHARDS and CHARLES R. HOOVER (*J. Amer. Chem. Soc.*, 1915, **37**, 108—113).—The molecular weight of sodium sulphate has been determined by the following method. A weighed amount of pure, fused sodium carbonate was treated in a platinum retort with a very slight excess of pure sulphuric acid; the solution was freed from carbon dioxide and evaporated in a quartz flask with the aid of a current of air, but without boiling, and the residual salt was fused and weighed. The ratio of the equivalent weights of sodium carbonate and sodium sulphate was found to be 1·00000 : 1·340155. From the value of the molecular weight of sodium carbonate, 105·995, when Ag = 107·880 (preceding abstract), the molecular weight of sodium sulphate was found to be 142·050. Calculating from this result, the atomic weight of sulphur becomes 32·060 (Na = 22·995; C = 12·005), which agrees well with the value 32·069 obtained by Richards and Jones (A., 1907, ii, 685) by the conversion of silver sulphate into the chloride. The mean of these two values, 32·065, is regarded as the most trustworthy value hitherto recorded.

In order to correct the weight of the sodium sulphate obtained

in the experiments to the vacuum standard, the density of the fused salt was determined, and found to be 2·698. E. G.

Method of Determining the Hydrates Formed by a Salt. H. W. Foote (*J. Amer. Chem. Soc.*, 1915, **37**, 288—292).—The method described in this paper depends on the fact that the addition of a sufficient quantity of sulphuric acid to a saturated solution of a hydrated salt with which the acid does not react causes the salt to crystallise either as a lower hydrate or in the anhydrous form. It is shown that in a series of solubility determinations of a salt with gradually increasing amounts of sulphuric acid, the presence of a pure salt is indicated by varying solubility and constant composition of the residue, whilst the presence of two salts as a mechanical mixture is indicated by constant solubility and a residue of variable composition. In this way, the detection of all the stable hydrates of a normal sulphate which form at a given temperature can be effected, except when an acid sulphate is formed before the anhydrous sulphate.

The method has been applied to the determination of the hydrates of copper sulphate at 25°, and the results are plotted as a curve showing the range of conditions under which each of the three hydrates, $CuSO_4,5H_2O$, $CuSO_4,3H_2O$, and $CuSO_4,H_2O$, is formed. The conditions for the trihydrate are very narrow; the pentahydrate has the widest range, being stable in contact with solutions containing as much as 49% of sulphuric acid. E. G.

Search for an Alkali Element of Higher Atomic Weight than Cæsium. Gregory Paul Baxter (*J. Amer. Chem. Soc.*, 1915, **37**, 286—288).—A large quantity of cæsium nitrate, prepared from pollucite, has been submitted to a prolonged fractional crystallisation, and the atomic weight of the metal in the least soluble fraction has been determined by the analysis of the chloride. The average result of the determinations gave the value 132·82, which agrees closely with that adopted by the International Committee on Atomic Weights, namely, 132·81. The experiments did not give any indication of the existence of an unknown alkali element, and thus confirmed the conclusion arrived at by Richards and Archibald (A., 1903, ii, 367), who worked with a much smaller quantity of material. E. G.

Solubility of Strontium Sulphate in Solutions of Calcium Salts. M. Raffo and G. Rossi (*Gazzetta*, 1915, **45**, i, 45—50).—The authors have determined the solubility, in calcium nitrate solutions of various concentrations, of strontium sulphate precipitated in the solution. The amount of strontium sulphate dissolved per 1 c.c. increases from 0·0483 gram for a 0·5% calcium nitrate solution to 0·1955 gram for a 6% solution. The solubility of barium sulphate in water is not affected by the presence of calcium chloride or nitrate. These results, obtained gravimetrically, were confirmed by measurements of the electrical conductivity. T. H. P.

Alloys of Zinc and Manganese. N. PARRAVANO [with, in part, U. PERRET] (*Gazzetta*, 1915, **45**, i, 1—6).—The author has made a thermal study of zinc–manganese alloys containing less than about 30% of manganese. The fusion diagram is similar to that of the zinc–iron alloys (compare von Vegesack, A., 1907, ii, 170), the two compounds $MnZn_7$ and $MnZn_3$ being formed. The alloys are hard and brittle; those containing 5—20% of manganese are porous, but those with a greater proportion of manganese are more compact. T. H. P.

Lithopone. W. J. O'BRIEN (*J. Physical Chem.*, 1915, **19**, 113—144).—Lithopone is an intimate mixture of barium sulphate and zinc sulphide precipitated by mixing solutions of barium sulphide and zinc sulphate. By special treatment, its physical properties are modified so that it becomes suitable for use as a pigment. Experiments have been made to ascertain the nature of the change which is involved in the darkening of lithopone, and also the conditions under which this colour change is retarded or inhibited.

It is found that zinc sulphide is reduced in a moist atmosphere under the influence of light, with the formation of metallic zinc and hydrogen sulphide. To prevent the darkening of the lithopone, it is necessary that the zinc sulphide should be covered by a protecting film. A lithopone of this character was obtained by producing a film of zinc oxide on the sulphide, the percentage of oxide varying from 3 to 5%. Aluminium oxide can be substituted for zinc oxide, and a film of sulphur retards the colour change. H. M. D.

Revision of the Atomic Weight of Cadmium. III. Electrolytic Determination of Cadmium in Cadmium Chloride. GREGORY PAUL BAXTER and MINER LOUIS HARTMANN (*J. Amer. Chem. Soc.*, 1915, **37**, 113—131).—Perdue and Hulett (A., 1911, ii, 397) Laird and Hulett (*Trans. Amer. Electrochem. Soc.*, 1912, **22**, 385), and Quinn and Hulett (A., 1914, ii, 127) determined the atomic weight of cadmium by methods of electrolytic deposition, and obtained the values 112·30, 112·31, and 112·29 respectively. Baxter and Hines (A., 1905, ii, 321), and Baxter, Hines, and Frevert (A., 1906, ii, 541) found the atomic weight of cadmium to be 112·417 and 112·418. In view of this discrepancy, determinations have now been made of the cadmium in the anhydrous chloride by direct electrolysis.

It has been found that cadmium material can be rapidly and efficiently purified by crystallisation of the bromide. A modified form of electrolytic cell with a mercury cathode is described, which was found to be very satisfactory for the direct electrolysis of cadmium chloride solutions.

The amount of cadmium in cadmium chloride was found to be 61·319%, as compared with 61·298% recorded by Quinn and Hulett (*loc. cit.*). The atomic weight of cadmium, calculated from this result, is 112·417 (Cl = 35·457), which agrees closely with the value found by Baxter, Hines, and Frevert from the analysis of

cadmium chloride by titration against pure silver. If the atomic weight of chlorine is taken as 35·458, that of cadmium becomes 112·421.

Cadmium bromide is being investigated by a similar electrolytic method, and these results also confirm the higher value for the atomic weight of cadmium. E. G.

Association of Mercuric Chloride in Water Solution. G. A. LINHART (*J. Amer. Chem. Soc.*, 1915, **37**, 258—274).—It is shown in this paper that the discordant results obtained in determinations of the molecular weight of mercuric chloride in aqueous solution, and the unusual behaviour of mercuric chloride in distribution ratio measurements, are due to the presence in the aqueous solution of double molecules of the salt.

It has been found that when a solution of mercuric chloride in benzene is shaken repeatedly with a saturated solution of sodium chloride, the mercuric chloride is completely removed owing to the formation of complexes, such as $NaHgCl_3$ and Na_2HgCl_4, which are practically insoluble in benzene. The mercuric chloride in such sodium chloride solutions can be readily estimated by precipitation with hydrogen sulphide.

This method of analysis has rendered it possible to prove the existence of double molecules of mercuric chloride in aqueous solution by measuring the distribution ratio of mercuric chloride between benzene and water at 25° and 40°. The equilibrium constants were found to be fairly concordant from extreme dilution to saturation for a given temperature, and it may therefore be assumed that Hg_2Cl_4 is the only complex in aqueous solutions at any concentration and at any temperature between 0° and 100°.

It is shown that the association of mercuric chloride in aqueous solutions can also be established from the results of Morse, and of Hantzsch and Vagt on the distribution ratio of mercuric chloride between water and toluene, from those of Biltz obtained by cryoscopic measurements, and from those of Kahlenberg, Landsberger, and Beckmann obtained by ebullioscopic determinations. E. G.

Electrolysis of Solutions of the Rare Earths. L. M. DENNIS and B. J. LEMON (*J. Amer. Chem. Soc.*, 1915, **37**, 131—137).—On the fractional electrolysis of a neutral solution of the nitrates of neodymium, praseodymium, lanthanum, and samarium, the lanthanum collects in the last fractions, and can thus be separated from the other earths of the didymium group. Lanthanum can be satisfactorily separated from praseodymium by this method. On the fractional electrolysis of the earths from xenotime, erbium collects in the early fractions and yttrium in the later fractions. The results of this work indicate that separations of some of the rare earths can be effected more rapidly and conveniently by this method than by the usual methods of fractional crystallisation and precipitation. E. G.

Physical Properties of the Metal Cobalt. HERBERT T. KALMUS and C. HARPER (*J. Ind. Eng. Chem.*, 1915, **7**, 6—17).—Pure cobalt, prepared by reduction of cobalt oxide (A., 1914, ii, 275), was

found to have D_4^{17} 8·7918 (unannealed), $D_4^{14·5}$ 8·8105 (annealed), $D_4^{16·5}$ 8·9253 (swaged); m. p., 1478°±1·1°; tensile strength, cast and unannealed, 34,400 lb. per sq. in., annealed, 36,980 lb. per sq. in., and, rolled, more than 100,000 lb. per sq. in.; compressive strength, cast and unannealed, 122,000 lb. per sq. in., annealed, 117,200 lb. per sq. in.; electrical resistance, 89·64 10 ohms per cm.^{3}; specific heat, from 0° to 890°, $0·1058 + 0·0000457t + 0·000000066t^2$. The hardness of cast cobalt is considerably greater than that of either iron or nickel, being approximately 124·0 (load 3500 lb.). The presence of from 0·06 to 0·3% of carbon in the metal increases the tensile and compressive strength and the electrical resistance, but has little effect on the hardness. Pure cobalt may be machined in a lathe as readily as pure iron or nickel, but it is somewhat brittle; cobalt containing a small quantity of carbon machines like mild steel, and, whilst pure cast cobalt cannot be rolled or swaged without developing cracks, cobalt containing carbon may be rolled or swaged down from cast bars to any extent provided that the metal is worked at a red heat.

W. P. S.

The Double Salts of Stannous and Potassium Chlorides. TOSHITSUNE FUJIMURA (*Mem. Coll. Sci. Kyoto*, 1914, **1**, 63—67).—A systematic investigation of the system $KCl–SnCl_2–H_2O$ at 25° has shown that the only double salts formed are those represented by $KCl,SnCl_2,H_2O$ and $2KCl,SnCl_2,2H_2O$. The solubility data are employed in the construction of a graph, in which the ratios $SnCl_2/H_2O$ and KCl/H_2O are plotted on rectangular axes. This graph shows clearly the limits of existence of the two double salts in contact with aqueous solutions.

H. M. D.

Mineralogical Chemistry.

Separation of the Constituents in a Natural Gas from which Gasolene is Condensed. GEORGE A. BURRELL and FRANK M. SIEBERT (*J. Amer. Chem. Soc.*, 1915, **37**, 392—396).—The authors' method for separating a natural gas into its constituent hydrocarbons by fractional distillation in a vacuum (A., 1914, ii, 741) has now been applied to the analysis of a natural gas obtained at a plant where it is treated for the commercial condensation of gasolene. The results showed that the gas consisted of methane, 36·8%; ethane, 32·6; propane, 21·1; butanes (chiefly), 5·8; pentanes and hexanes, 3·7%. In addition, about 1·0% of nitrogen and 0·03% of carbon dioxide were present, but were left out of calculation in the analysis. E. G.

Lawsonite from the Central Coast Ranges of California. AUSTIN F. ROGERS (*Amer. J. Sci.*, 1915, [iv], **39**, 105—112).—A brief summary is given of the literature of lawsonite. Two distinct

modes of occurrence are recognised: (1) as a secondary mineral in slightly altered or saussuritised diorites and gabbros (California, Corsica, Piedmont, Gorgona, New Caledonia); (2) as an accessory or essential constituent of schists and gneisses, which usually contain glaucophane (California, Corsica, Piedmont, Hautes-Alpes). Several new occurrences are described from Santa Clara and Alameda Counties in California. Crystals from Arroya Mocho in Alameda County, analysed by H. L. SMALL, gave the following results, agreeing with the usual formula $H_4CaAl_2Si_2O_{10}$:

SiO_2.	Al_2O_3.	CaO.	CO_2.	H_2O.	Total.
38·10	32·21	17·74	1·12	10·85	100·02

L. J. S.

Meteoric Iron from Sams Valley, Oregon. W. M. FOOTE (*Amer. J. Sci.* [iv], 1915, **39**, 80—86).—This mass of iron, weighing nearly 7 kilos., was found in 1894 in the Sams Valley, Jackson County, Oregon. The crystalline structure is that of a medium octahedrite. D 7·794. Analysis, by J. E. WHITFIELD, of the nickel-iron (93·781% of the mass) gave I, and of the schreibersite (6·194%) the results under II:

	Fe.	Ni.	Co.	Cu.	C.	P.	S.	Si.	Total.
I.	89·357	9·762	0·682	0·017	0·016	nil	0·059	0·009	99·992
II.	65·13	20·93	—	—	—	13·94	—	—	100·00

This composition is very similar to that of the Mount Edith meteoric iron from Western Australia (A., 1914, ii, 481).

L. J. S.

Physical and Chemical Constants of Mineral Waters. F. BORDAS (*Ann. Falsif.*, 1914, **7**, 387—407).—Results of examinations of French mineral waters are given, the following constants being recorded: refractive index, capillary pressure, freezing point, electrical resistance and conductivity, ionisation, and estimation of the total solids, alkalinity, chlorine, nitric nitrogen, and various elements characteristic of the waters. W. P. S.

Analytical Chemistry.

New Method for Estimation of Acidity. I. Traube and R. Somogyi (*Intern. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 479—484).—The method is based on the observation that the addition of a strong capillary-inactive acid (a strong acid which, on dissolving in water, does not lower the surface tension of the solvent) to the capillary-inactive salt of a weaker capillary-active acid sets the weak capillary-active acid free and causes a lowering of surface tension, from which the quantity of strong acid added can be calculated.

The capillary-inactive salt chosen for employment was the sodium salt of *iso*valeric acid, and the mode of operation for the estimation of the acidity of various human and animal blood-sera and other tissue fluids was to mix 5 c.c. of a 2% solution of sodium *iso*valerate with 0·2 c.c. of serum or other fluid and measure the lowering of surface tension by the viscostagonometer at 23°.

The results are tabulated and compared with the corresponding alkalinities obtained by Traube's method (this vol., i, 95).

H. W. B.

Determination of Very Weak Acids and Bases by Means of Electrolytic Conductivity Measurements. SHINKICHI HORIBA (*Mem. Coll. Sci. Kyoto*, 1914, **1**, 35—47).—The electrical conductivities of mixtures of aniline and hydrochloric acid and of phenol and sodium hydroxide have been determined in dilute aqueous solution at 25°. Empirical formulæ have been deduced, which represent the change in conductivity with change in the relative proportions of acid and base. It is shown that the change in the conductivity may be applied to the estimation of weak acids and bases which cannot be estimated by the ordinary methods of alkalimetry or acidimetry. In the case of aniline and hydrochloric acid, the concentration of aniline in a solution containing 0·02 to 0·04 mol. of acid per litre is given by the equation $C = -(K_m - K_a)/0{\cdot}2895$, in which K_a is the conductivity of the pure acid solution, and K_m that of the solution which contains in addition C mols. of aniline per litre. The concentration of the phenol in a sodium hydroxide solution is related to the change in the conductivity in a similar way, but the denominator varies with the concentration of sodium hydroxide solution in accordance with the equation:

$$C = -(K_m - K_b)/(0{\cdot}154 + 0{\cdot}0433C_b^{\frac{1}{2}}),$$

in which K_b and C_b represent the conductivity and concentration of the pure sodium hydroxide solution, K_m that of the solution which contains in addition C mols. of phenol per litre. The formula may only be applied to solutions for which C_b lies between 0·02 and 0·04 mol. per litre, and the concentration of phenol must be less than $\frac{1}{2}C_b$.

The conductivity data give the mean value of $2{\cdot}50 \times 10^{-5}$ for the hydrolysis constant of aniline hydrochloride and $0{\cdot}95 \times 10^{-4}$ for sodium phenoxide.

H. M. D.

Standardisation of Alkalimetric Solutions. FRANCIS D. DODGE (*J. Ind. Eng. Chem.*, 1915, **7**, 29—30).—Potassium hydrogen phthalate is recommended for use in standardising alkali solutions. The salt has the formula $KHC_8H_4O_4$, is stable, non-hygroscopic, soluble in water, has a high molecular weight, and may be prepared readily from phthalic anhydride and potassium hydroxide.

W. P. S.

New Chemical Hygrometer. ERIC K. RIDEAL and A. HANNAH (*Analyst*, 1915, **40**, 48—54).—The principle of the apparatus described depends on the fact that sulphuric acid will completely remove the moisture from air at one contact, which is not the case with

solid dehydrating substances. The apparatus consists essentially of two bulbs of equal capacity (about 20 c.c.) provided at their lower ends with mercury reservoirs; above the surface of the mercury in one of the bulbs is placed a small quantity of sulphuric acid, and the acid ocupies a bulb above the main bulb when this is filled with mercury. The upper stem of the other bulb is graduated, and the upper stems of both bulbs are connected through a tube carrying a three-way tap, this tube also carrying an aniline U-gauge provided with a bulb. The sample of air is drawn into the bulb provided with the graduated stem, then passed into the sulphuric acid bulb, and the diminution in volume ascertained from the volume of mercury in the other bulb W. P. S.

Detection of Bromides in Presence of Thiocyanates, Cyanides, and Ferrocyanides. Louis J. Curtman and Alan G. Wikoff (*J. Amer. Chem. Soc.*, 1915, **37**, 298—301).—Experiments have been made to determine the extent to which thiocyanates, cyanides, and ferrocyanides interfere with the detection of bromides by means of chlorine water. The following method has been devised which is capable of detecting 2 mg. of bromine in presence of 500 mg. of any of these interfering substances.

The solution to be tested, which should be either neutral or slightly acidified with sulphuric acid, is treated with 15 c.c. of a saturated solution of sulphur dioxide. The solution is heated until it boils, and, whilst still hot, an excess of 2*N*-copper sulphate solution is slowly added with constant stirring. The hot solution is filtered, the precipitate washed twice with water, and the washings are added to the filtrate, which is then concentrated to about 5—10 c.c. The liquid is cooled and transferred to a test-tube, treated with 1 c.c. of 3*N*-sulphuric acid and 1 c.c. of 1% potassium permanganate, and shaken. About 0·5 c.c. of carbon disulphide is now added, and the mixture again shaken. If the carbon disulphide becomes yellow, the presence of bromine is indicated. The test can be carried out completely in about fifteen minutes. Numerous tests have been made, which prove that the method is trustworthy.

E. G.

Estimation of Iodine in Pharmaceutical Preparations. Ch. Lormand (*Ann. Falsif.*, 1914, **7**, 432—441).—The author discusses the methods given in the French codex for the estimation of iodine in pharmaceutical preparations; in a few cases the method to be used is not prescribed. In the case of tincture of iodine, the official method simply estimates the free iodine, and does not take into account the hydriodic acid which is always formed, although directions are given to test for the presence of this acid. The total quantity of iodine in this tincture may be estimated by treating 5 grams of the sample with sodium hydrogen sulphide, neutralising the excess of the latter with sodium hydroxide, acidifying the solution with nitric acid, and precipitating the iodide with silver nitrate. It is pointed out that a portion of the iodine in iodine–iodide ointment enters into combination with the fatty constituents, and

that the iodine content diminishes gradually with time for this reason. Iodine in iodo-tannin-phosphated wines may be estimated by treating the wine with an excess of milk of lime, filtering, acidifying the filtrate with nitric acid, and precipitating the iodide with silver nitrate. W. P. S.

Use of Mercuric Salts for the Detection of Sulphur Dioxide in the Atmosphere. G. Denigès (*Ann. Chim. anal.*, 1915, **20**, 10—11; from *Bull. Soc. pharm. Bordeaux*, 1914).—The reagents yielding the best results are: (1) 5 grams of mercuric oxide dissolved in 20 c.c. of sulphuric acid (D 1·84) and 100 c.c. of water; (2) 5 grams of mercuric acetate dissolved in 100 c.c. of water containing 1 c.c. of glacial acetic acid; (3) 5 grams of mercuric nitrate dissolved in 5 c.c. of nitric acid (D 1·39) and 50 c.c. of water. A glass rod is dipped in any one of the reagents, then exposed in the atmosphere to be tested, and its surface, after the exposure, examined under the microscope. Characteristic crystals will be observed if the atmosphere contains even minute quantities of sulphur dioxide. W. P. S.

Gaseous Impurities in the Air of Railway Tunnels. Atherton Seidell and Philip W. Meserve (*U.S. Public Health Service, Hygienic Lab. Bull.* No. 92, 1914, pp. 1—47).—Eighty-eight samples of air from railway tunnels in the city of Baltimore were examined; those from tunnels through which steam locomotives passed contained on an average 15·1 parts of sulphur dioxide and 267 parts of carbon monoxide per million parts of air, whilst the corresponding figures for a tunnel on an electrified railway were 2·9 and 25 parts respectively. A review of the available literature on the physiological effects of small amounts of these two gases showed that the concentrations of the gases which produce an unmistakable harmful effect are somewhat greater than the maximum amounts which were found in the samples of tunnel air examined. On account of the particular conditions under which the investigation was made, methods based on the aspiration of the sample of air through a small volume of liquid followed by a gravimetric or volumetric estimation of the retained sulphur dioxide could not be used, but trustworthy results were obtained by direct titration with $N/1000$-iodine solution after applying a correction (compare A., 1914, ii, 484). When the samples of air were kept in moist bottles, practically the whole of the sulphur dioxide disappeared within one hour; in dry bottles the loss during the first two hours was usually very small, although in the case of very small quantities of the gas an appreciable loss was noticed within thirty minutes. Of small amounts of sulphur dioxide liberated in a closed room only about 30—60% could be recovered. The iodine pentoxide method (A., 1908, ii, 66) was used for the estimation of the carbon monoxide, special bulbs, having narrow connecting tubes, being employed for the absorption of the resulting carbon dioxide and liberated iodine, and the closed aspiration system was adopted in passing the sample of air through

the apparatus. Analyses of test mixtures of very small quantities of carbon monoxide with air showed that from 88% to 98% of the former could be recovered. W. P. S.

The Folin–Farmer Method for the Colorimetric Estimation of Nitrogen. JOSEPH C. BOCK and STANLEY R. BENEDICT (*J. Biol. Chem.*, 1915, **20**, 47—59).—The Folin-Farmer method contains certain sources of error. The results usually agree with the Kjeldahl method within 2 or 3%; the latter method generally gives the higher result, but variations between +4 and −11·8 occur. Some modifications are suggested. W. D. H.

Comparison of the Gunning Copper Method and the Kjeldahl–Gunning–Arnold Method for the Estimation of Nitrogen OVE F. JENSEN (*J. Ind. Eng. Chem.*, 1915, **7**, 38—39).—With dried blood the period of digestion in the Gunning copper method should be continued for two hours in order to convert the whole of the nitrogen into ammonia, whilst one hour's digestion is sufficient in the Kjeldahl-Gunning-Arnold method. In the case of numerous other substances examined, a digestion of one and a-half hours was sufficient for either method. The Gunning copper method (use of copper sulphate and potassium sulphate) has the advantage over the Kjeldahl-Gunning-Arnold method (mercury and potassium sulphate) in that the addition of potassium sulphide is unnecessary in the distillation of the ammonia; further, in adding the sodium hydroxide solution before distilling, the copper sulphate acts as an indicator, and a large excess of alkali may be avoided. W. P. S.

Rapid Method of Estimating Nitrates. EDMUND KNECHT (*J. Soc. Chem. Ind.*, 1915, **34**, 126—127).—The process is based on the discovery that nitrates are reduced to ammonia quantitatively and almost instantaneously by titanous hydroxide. A solution of the nitrate (in amount about equivalent to 0·1 gram of potassium nitrate) is treated in a copper flask with an excess of sodium hydroxide and about 20 c.c. of commercial titanous sulphate or chloride. The ammonia produced is removed by distillation. The process is also trustworthy for the estimation of nitrites. C. S.

Comparison of a Few Methods for the Estimation of Total Phosphoric Acid in Superphosphate. C. A. PETERS (*J. Ind. Eng. Chem.*, 1915, **7**, 39—40).—The official (American) method for estimating total phosphoric acid in superphosphate gives too high results unless silica is removed previously by evaporating the solution to dryness, treating the residue with dilute nitric acid, and filtering the solution. Other methods, such as that described by Baxter (A., 1903, ii, 180), Pemberton's volumetric method, and direct precipitation as ammonium magnesium phosphate in the presence of ammonium citrate, yield trustworthy results.
W. P. S.

Destruction of Organic Substances in Urine by Hydrogen Peroxide. C. E. CARLSON (*Ann. Chim. anal.*, 1915, **20**, 16—17; from *Svensk. farm. Tidscrift*, 1914, **65**).—In testing urine for arsenic, mercury, etc., the preliminary operation for the destruction of the organic substances may be carried out by treating 500 grams of the sample with an equal weight of 15% hydrogen peroxide solution, and evaporating the mixture to dryness; the residue is then transferred to a flask, boiled with several successive quantities of 25 c.c. of hydrogen peroxide, and again evaporated to dryness. The residue is heated slightly, and if any appearance of charring is noticed the treatment with hydrogen peroxide is repeated. The final residue is then heated at 300° to expel ammonium salts.

W. P. S.

Volumetric Estimation of Silver. C. DEBRUN (*Ann. Falsif.*, 1914, **7**, 407—409).—The strength of the sodium chloride solution used in the Gay-Lussac method for the titration of silver is so adjusted that, at 15°, 100 c.c. of the solution are equivalent to 1 gram of silver; if used at other temperatures, the silver-value of the solution is altered; thus, at 0°, 100 c.c. of the solution (measured at 15°) will measure 99·953 c.c.; at 5°, 99·938 c.c.; at 10°, 99·956 c.c.; at 20°, 100·092 c.c.; at 25°, 100·205 c.c.; at 30°, 100·328 c.c.; and at 35°, 100·484 c.c. W. P. S.

Electrolytic Separation of Zinc, Copper and Iron from Arsenic. A. K. BALLS and C. C. MCDONNELL (*J. Ind. Eng. Chem.*, 1915, **7**, 26—29).—Zinc, iron, and copper may be separated electrolytically from arsenic by using an electrolyte containing a large excess of potassium hydroxide. The arsenic must always be present in the higher state of oxidation. The mixture of the metal and arsenic is dissolved in 50% potassium hydroxide solution (tartaric acid is added in the case of iron and copper), an excess of about 20 grams of the alkali is added, the mixture is diluted to 95 c.c. and submitted to electrolysis, a nickel basin being used for the cathode and a rotating platinum paddle for the anode. The addition to the electrolyte of 0·2 gram of potassium nitrate renders the deposit of zinc more smooth and adherent, whilst 2 grams of the nitrate may be added in the case of copper without appreciably interfering with the accuracy of the separation. The arsenic may be estimated in the solution from the electrolysis. W. P. S.

Estimation of Copper and Lead in Babbitt Metal. E. W. HAGMAIER (*Met. and Chem. Eng.*, 1914, **12**, 753; from *J. Soc. Chem. Ind.*, 1915, **34**, 87).—To 1 gram of the alloy 15 c.c. of hot water and sufficient tartaric acid are added to keep the tin and the antimony in solution; 5 c.c. of nitric acid are added, and the liquid is boiled until solution is complete. The solution is heated with 5 c.c. of sulphuric acid until nitrous fumes cease to be evolved, charring being avoided. The mixture is cooled, 50 c.c. of water are added, and the lead sulphate is filtered off. The filtrate is diluted to 400—500 c.c., and after the addition of 1—2 c.c. of hydrochloric

acid the copper is precipitated on a strip of pure aluminium, and is estimated in the usual manner. C. S.

Separation and Estimation of Aluminium Associated with Iron, by the Action of Acetyl Chloride in Acetone. H. D. MINNIG (*Amer. J. Sci.*, 1915, [iv], **39**, 197—200).—Aluminium chloride is precipitated completely, as the hydrated compound, $AlCl_3,6H_2O$, when its concentrated solution is mixed with a solution of 1 part of acetyl chloride in 4 parts of acetone; ferric chloride remains soluble under these conditions. The solution containing aluminium chloride and ferric chloride is evaporated to the smallest possible volume, then cooled to 15°, 20 c.c. or more of the acetyl chloride–acetone mixture are added drop by drop, the precipitate is collected, dried, and converted into oxide by ignition. The iron may be estimated in the filtrate by precipitation as hydroxide. The acetyl chloride employed should be free from phosphorus compounds; these are frequently present in ordinary acetyl chloride, and cause the iron results to be too high owing to the formation of ferric phosphate. W. P. S.

Reduction of Ferric Sulphate in Acid Solution by Means of Cadmium Amalgam for Titration of Iron and Free Sulphuric Acid. J. H. CAPPS and O. W. BOIES (*J. Physical. Chem.*, 1915, **19**, 65—75).—In addition to the substances which are usually found in naturally occurring waters, mine waters frequently contain free sulphuric acid and ferrous and ferric iron. On account of the hydrolysis of the ferric salt, the free sulphuric acid cannot be estimated by titration with alkali, and the application of the hydrogen electrode method yields unsatisfactory results by reason of the influence of the platinised platinum electrode on the ferrous–ferric equilibrium.

A satisfactory method for the estimation of the iron and the free sulphuric acid in waters of this type has been worked out. This involves the reduction of the ferric iron to ferrous by the action of cadmium amalgam. The water is placed in a small flask provided with a two-holed rubber stopper, through which passes a separating funnel for the admission of the amalgam and a tube for connecting the flask with a vacuum pump. The air in the flask, as well as that in solution, is removed by exhaustion. Hydrogen is then admitted, and the amalgam run into the water. After shaking for thirty to sixty seconds, the ferric iron is reduced and the free acid can be titrated with sodium carbonate solution with methyl-orange as indicator. Titration of the reduced solution with standard permanganate gives the total iron, whilst ferrous iron is obtained by titration of the original water. H. M. D.

Separation of Tungsten from Molybdenum. EDWARD ELLSWORTH MARBAKER (*J. Amer. Chem. Soc.*, 1915, **37**, 86—95).—The following method for the quantitative separation of tungsten and molybdenum is based on Mdivani's method of estimating tungsten (A., 1911, ii, 230).

The solution containing sodium tungstate and molybdate is heated to boiling and treated with a solution containing 50 grams of stannous chloride ($SnCl_2,2H_2O$) in 200 c.c. of concentrated hydrochloric acid. The amount of the reagent must be carefully regulated, and should be used in the proportion of 20 c.c. for each 0·15 gram of tungsten trioxide. The volume of the solution for analysis should be kept between 60 c.c. and 300 c.c. according to the quantity of tungsten present. After the mixture has been boiled for a few minutes, the blue precipitate (W_2O_5) is allowed to subside, and the supernatant liquid is filtered. The precipitate is washed with hot 5% hydrochloric acid until the washings are free from molybdenum. The precipitate is collected on the filter and allowed to drain, and the filter is then ignited gently in a porcelain crucible. The resulting tungsten trioxide is cooled in a desiccator and weighed.

The filtrate and washings are united and evaporated to a small volume. If a large amount of molybdenum is present, the solution is diluted to 250 c.c. To 50 c.c. of this solution 5—10 grams of 20-mesh zinc are added. The tin separates as metal, and when the precipitation is complete, the solution is filtered, and the tin is washed several times with hot water. The washings are added to the filtrate and heated to 60°. The reductor flask is charged with 20 c.c. of 10% ferric ammonium sulphate and 20 c.c. of the "titrating solution" (consisting of 90 grams of manganous sulphate, 650 c.c. of water, 175 c.c. of syrupy phosphoric acid, and 175 c.c. of concentrated sulphuric acid). Fifty c.c. of dilute hydrochloric acid (containing 2·5% of the concentrated acid) are passed through the reductor, followed by the solution containing the molybdenum, and then by 150 c.c. of the dilute hydrochloric acid, and finally by 150 c.c. of hot water. The solution in the flask is now titrated with 0·1*N*-potassium permanganate, and, from the result obtained, the amount of molybdenum present is calculated (compare Randall, A., 1907, ii, 912).

The quantity of tungsten in a sodium tungstate solution can be estimated by Mdivani's method if sodium chloride is previously added. E. G.

Use of Bettendorf's Reagent in Testing the Purity of Drugs Containing Antimony. Alfredo Pagniello (*Boll. Chim. Farm.*, 1914, **53**, 689—691).—The fact that certain antimony drugs give precipitates with Bettendorf's reagent, which consists of stannous chloride and hydrochloric acid, is shown to be due to reduction of the antimony compounds to metallic antimony, and not to the presence of arsenic derivatives as impurities.

Pharmaceutical products containing antimony may, however, be examined for the presence of arsenic by means of the official test given in the "Deutsches Arzneibuch" for antimony pentasulphide: 0·5 gram of the latter is heated for two minutes at 50—60° and stirred with 5 c.c. of aqueous ammonium carbonate solution saturated in the cold; acidification of the filtered liquid with hydrochloric acid should not be followed by formation of yellow arsenical

flakes within six hours. In the case of any other antimony compound, the latter is converted into the pentasulphide, which is separated by filtration, and then purified by dissolution in ammonium sulphide solution and precipitation by means of hydrochloric acid. The purified pentasulphide is then digested with ammonium carbonate solution, as described above. T. H. P.

Titanium Trichloride in Qualitative Analysis. A. MONNIER (*Ann. Chim. anal.*, 1915, **20**, 1—4).—Titanium trichloride may be used as a reagent for the identification of certain metals and organic acids, the reactions depending on the reducing property of the reagent. Platinum, iridium, and palladium chlorides are reduced when heated with titanium trichloride solution, a black precipitate of the metal being formed; gold chloride is reduced in the cold with the formation of a blue coloration. Tungstates give a blue coloration, and molybdates a brown colour, which changes to green or blue when the mixture is heated. Vanadates are decolorised by titanium trichloride, but a blue coloration develops on heating. Chromates and dichromates are reduced to green chromium compounds, selenious acid gives a red precipitate of selenium, and telluric acid is reduced when heated with the reagent. All these reactions take place most readily in dilute hydrochloric acid solution. Sulphur is deposited when sulphurous acid, sulphites, or thiosulphates are treated with titanium trichloride. The following reactions occur when salts of various organic acids are heated with titanium trichloride solution: Formates and acetates, violet-black precipitates; oxalates, yellowish-brown precipitate; succinates, violet precipitate; tartrates, grey precipitate; lactates, blue coloration, no precipitate; benzoates, brownish-green precipitate; salicylates, yellow precipitate; tannin, reddish-orange precipitate. A characteristic violet coloration is obtained when a citrate solution is boiled with titanium trichloride; this coloration is not affected by the presence of formic, acetic, succinic, lactic, and benzoic acids, citric acid inhibiting the reactions given by these acids. Oxalic and salicylic acids, however, interfere with the reaction yielded by citric acid. W. P. S.

Estimation of Organic Matter in Potable Water. J. D. FILIPPO and H. J. BACKER (*Chem. Weekblad*, 1915, **12**, 73—78).—Carbohydrates and other organic matter present in water are oxidised to oxalic acid by permanganate in alkaline solution. To avoid the error thus introduced, the solution should be acidified before determining the excess of permanganate by titration by the iodometric method. A. J. W.

Separation of the Illuminants in Mixed Coal and Water Gas. G. A. BURRELL and I. W. ROBERTSON (*J. Ind. Eng. Chem.* 1915, **7**, 17—21).—The following results were obtained on the analysis of a gas consisting of 1 part of carburetted water-gas and 3 parts of coal-gas, the method used being that described by Burrell and Seibert (A., 1914, ii, 741), in which the various gases are separated from each other by fractional distillation at low

temperatures; the figures in parentheses show the figures found by ordinary methods of analysis: Carbon dioxide, 2·63 (2·64); oxygen, 0·81 (0·81); carbon monoxide, 13·25 (13·34); hydrogen, 37·33 (37·04); methane, 31·13 (30·96); ethane, 2·10 (1·82); nitrogen, 4·23 (4·72); propane, 0·43; ethylene, 6·05; propylene, 0·60; butylene, 0·11; benzene, 1·33; (illuminants, 8·67). A method is described for the estimation of benzene in coal gas; after water-vapour has been removed from the gas, the latter is cooled to −78°, and as much gas is removed as possible by means of a pump, the cooling medium being then removed and the condensed liquid vaporised. The pressure obtained, compared with the original pressure of the gas, gives the quantity of benzene in the gas. W. P. S.

Method for the Estimation of Glycerol in Pharmaceutical Preparations. C. H. Briggs (*Pharm. J.*, 1915, **94**, 157; *J. Amer. Pharm. Assoc.*, 1915).—A quantity of the preparation containing about 2 grams of glycerol is mixed with 0·5 gram of magnesium oxide and 75 c.c. of santal oil and distilled under reduced pressure until about two-thirds of the oil has been distilled. The condenser is then rinsed with 100 c.c. of light petroleum, next with 5 c.c. of water, both of these are added to the distillate, and the aqueous portion is separated. The oil solution is now shaken three times in succession with 5 c.c. of water, the united aqueous extracts are shaken with 30 c.c. of light petroleum to remove any traces of oil, the aqueous solution being then evaporated below 50°, and the residue of glycerol dried for twenty-four hours under reduced pressure over sulphuric acid. W. P. S.

Detection and Estimation of Free or Combined Glycerol. Application to Glycerophosphates. Estimation of Phosphorus in Glycerophosphates. M. François and E. Boismenu (*J. Pharm. Chim.*, 1915, [vii], **11**, 49—68).—Glycerol may be identified by heating it with potassium hydrogen sulphate, acraldehyde being formed; if the acraldehyde vapours are passed into magenta-sulphurous acid reagent, a red coloration is obtained, which changes to blue when the solution is heated. Combined glycerol in glycerophosphates may be identified by the same means. The dichromate method is recommended for the estimation of glycerol; a large excess of dichromate should be employed, the mixture of glycerol and dichromate solution must be acidified with concentrated sulphuric acid, and the oxidation continued for two hours at a boiling temperature. The same method may be used directly for the estimation of glycerol in glycerophosphates. Phosphorus is estimated in the latter by heating the substance for two hours with potassium dichromate and sulphuric acid, reducing the excess of dichromate with sodium sulphite, then adding sodium acetate and precipitating the phosphoric acid with molybdic acid reagent. The ammonium phosphomolybdate is next converted into ammonium magnesium phosphate, and weighed as magnesium pyrophosphate. W. P. S.

Reaction of β-Naphthol. J. KATAYAMA and B. IKEDA (*J. Pharm. Chim.*, 1915, [vii], **11**, 73—74; from *Yakugakuzasshi*, 1914).—A violet coloration is obtained on adding 0·05 c.c. of a 0·01% sodium nitrite solution to 1 c.c. of a β-naphthol solution mixed with a few drops of concentrated sulphuric acid. The reaction may be obtained with 0·0002 gram of β-naphthol per c.c. of solution.

W. P. S.

Volumetric Fehling Method using a New Indicator. A. M. BRECKLER (*J. Ind. Eng. Chem.*, 1915, **7**, 37—38).—The method described depends on a constant volume of solution at the end of the titration, a constant time of boiling, and the use of sodium sulphide solution as an external indicator. A preliminary titration gives approximately the quantity of the sugar solution required to reduce 10 c.c. of Fehling's solution; towards the end of the titration a drop of the solution is added to a drop of 4% sodium sulphide solution, the end of the titration being denoted by the drop remaining colourless after the suspended cuprous oxide has turned black and settled as a precipitate. Ten c.c. of Fehling's solution are then mixed with about 97% of the quantity of sugar solution used in the preliminary experiment and sufficient water to make the final volume up to 30 c.c., the mixture is boiled for one and a-half minutes, and the titration completed, which can usually be done by two additions of the sugar solution.

W. P. S.

Estimation of Sugar in Small Quantities of Blood. ROBERT C. LEWIS and STANLEY R. BENEDICT (*J. Biol. Chem.*, 1915, **20**, 61—72).—The estimation of sugar in human blood in cases of diabetes is most necessary; a review of previous methods is given. The new method proposed is performed with 2 c.c. of blood, and is colorimetric, the reagents added being picric acid and sodium carbonate; the picric acid is added first to the blood, previously laked with water; this precipitates all the protein and no sugar; the sodium carbonate is then added to the filtrate, which is evaporated until precipitation occurs, water is added, and the liquid again heated to boiling, made up to volume, and filtered into the colorimeter chamber. The figures given show that the method is trustworthy. Any traces of creatinine in the blood are insufficient to affect the colour values. The normal percentage of dextrose in human blood is 0·09 to 0·11, average 0·1%.

W. D. H.

Estimation of Formic Acid in Ketchup. C. A. PETERS and L. P. HOWARD (*J. Ind. Eng. Chem.*, 1915, **7**, 35—37).—From 91 to 92% of the formic acid added to ketchup can be obtained by Fincke's process (A., 1911, ii, 282; 1913, ii, 442); 1000 c.c. of distillate should be collected, and the formic acid retained in an intermediate flask containing calcium carbonate and water.

W. P. S.

Influence of Hydroxy-acids and Lactones on Determinations of the Chemical Constants of Fatty Acids. C. A. BROWNE (*J. Ind. Eng. Chem.*, 1915, **7**, 30—34).—The author discusses the influence of hydroxy-fatty acids, particularly those having a pronounced tendency to form lactones, on the estimation of the acid, saponification, ester, and acetyl numbers of fatty acid mixtures.
W. P. S.

Estimation of Potassium Hydrogen Tartrate and Tartaric Acid. H. ASTRUC (*Ann. Falsif.*, 1914, **7**, 416—417).—The racemate method (A., 1910, i, 651; ii, 359; 1911, ii, 666) is recommended as being trustworthy. W. P. S.

Estimation of Total Tartaric Acid and Potassium in Wines. A. KLING and A. LASSIEUR (*Ann. Falsif.*, 1914, **7**, 410—416).—The total quantity of tartaric acid in wine may be estimated rapidly by the following modification of the racemate method (A., 1911, ii, 666). Twenty-five c.c. of the wine, 10 c.c. of a 2% ammonium *l*-tartrate solution, and 20 c.c. of a solution containing 16 grams of calcium carbonate and 120 c.c. of glacial acetic acid per litre, are mixed, and, after thirty minutes, the precipitate of calcium racemate is collected, washed, dissolved in dilute sulphuric acid, and the solution titrated with potassium permanganate solution. Potassium is estimated by the perchlorate method. The ash of the wine is treated with a few drops of water and a small quantity of perchloric acid solution, the mixture is evaporated to remove the greater part, but not all, of the excess of perchloric acid, the residue is mixed with alcohol, collected on a filter, and washed with alcohol. This residue, containing the potassium perchlorate, is then heated with sodium carbonate, and the resulting chloride is titrated by Volhard's process. The method estimates the potassium present in the wine in the form of salts of organic acids and as sulphate. W. P. S.

Determination of the Freezing Point of Milk. J. J. VAN ECK, J. D. FILIPPO, F. H. VAN DER LAAN, A. LAM, A. VAN RAALTE, and L. TH. REICHER (*Chem. Weekblad.*, 1915, **12**, 108—116).—Determinations of the freezing point of a number of samples of milk have proved that the method of Dekhuyzen and that of the Dutch "Codex alimentarius" yield equally trustworthy results.
A. J. W.

Analysis of Butter (Estimation of Water). ISNARD (*Ann. Falsif.*, 1914, **7**, 442—443).—The amount of water in butter may be estimated by separating the aqueous portion (containing the casein, etc., in suspension) from the fat, evaporating it, and weighing the dry residue. The sum of the weights of this residue and of the fat subtracted from the weight of the butter taken for the estimation gives the quantity of water present. W. P. S.

Spermaceti: Its Solidifying and Melting Point. ROBERT MELDRUM (*Chem. News*, 1915, **111**, 37—39).—The following results were obtained in the determination of the solidifying point of spermaceti by various methods: Dalican's method, 45·75°; in small-bore tube, 45·75°; by slow cooling, 45·75° to 45·95°; by continuous stirring, 45·75°; by opacity method, 45·8° to 46·0°; by capillary, 44·7° to 45·0°. Determinations of the m. p. were also made by different methods, namely, thermometer-bulb method, 45·3° to 45·5°; open capillary, 45·1° to 45·4°; closed capillary, 45·9° to 46·0°; opacity method, 46·0° to 46·4°. Previous repeated heating of the spermaceti at 100° and cooling does not affect the solidifying point; further, this constant is not affected by the presence in the spermaceti of 0·1% of water, glycerol, or oleic acid. The presence of 5% of sperm oil lowers the solidifying point by about 0·2°. W. P. S.

Method for the Estimation of Unsaponifiable Matter Applicable to Ether Extracts, Fats, Oils, and Waxes. J. B. RATHER (*J. Ind. Eng. Chem.*, 1915, **7**, 34—35).—In the method described, the fatty acids are removed from the unsaponifiable substances by precipitation from ethereal solution. A quantity of about 0·4 gram of the fat is boiled in a flask for one hour with 20 c.c. of 2*N*-alcoholic sodium hydroxide solution, the mixture is evaporated nearly to dryness and the residue is treated with 3·5 c.c. of glacial acetic acid, 50 c.c. of ether, and 25 c.c. of water. When the residue has dissolved, the solution is transferred to a separating funnel, and the flask is rinsed with five successive quantities of 20 c.c. of ether. The aqueous layer is then drawn off, the ethereal solution is shaken twice with 10 c.c. of 33% sodium hydroxide solution and 25 c.c. of warm water, and next with five successive quantities of 30 c.c. of cold water. The ethereal solution is then evaporated in a weighed flask, the residue dried at 100°, and weighed. To correct for a small quantity of fatty acids retained by the unsaponifiable substances, the residue is dissolved in ether, the solution shaken with hydrochloric acid, the ethereal solution is again evaporated to dryness, the residue dissolved in alcohol and titrated with *N*/10-sodium hydroxide solution; the number of c.c. of the latter required is multiplied by 0·028, and the result deducted from the weight found previously. W. P. S.

Substances which Mask the Colour Reactions of Strychnine. EFISIO MAMELI (*Boll. Chim. Farm.*, 1914, **53**, 366—369).—Otto's reaction for strychnine consists in the formation of violet streaks in sulphuric acid solution in contact with crystals of potassium dichromate, and Mandelin's reaction in the formation of a bluish-violet coloration, changing to violet-red, and, later or on addition of water, to red, with a sulphuric acid solution of ammonium vanadate. The following compounds, if present in large proportion, entirely prevent the appearance of these reactions, or, if present in quantities small in comparison with that of the alkaloid, weaken the reactions considerably: phenacetin, migranin

(mixture of antipyrine, caffeine, and citric acid), *o*- or *p*-phenetidine, *p*-aminophenol, "phenocoll," salacetol, protocatechuic acid, aminomethylenecatechol, dormiol (amylenechloral), guaiacol, acetylguaiacol, *p*-iodoguaiacol, heroine (diacetoxymorphine), helmitol (hexamethylenetetramine anhydromethylenecitrate), pyramidone, zinc phenolsulphonate, glycerol, and hydrochloric acid. Both reactions are inhibited by even small proportions of phenol, anisole, phenetole, β-naphthol, β-naphthyl salicylate, β-naphthyl benzoate, and *p*-phenetylcarbamide. Otto's reaction is prevented by a small amount of acetylacetone or phenyl salicylate, but larger quantities of these are necessary to interfere with the action of Mandelin's reagent, which then gives a green coloration. Aniline, acetic acid, tartaric acid, methylethyldimethylaminomethylcarbinyl benzoate hydrochloride, and hexamethylenetetramine do not disturb Mandelin's reaction, but diminish the intensity of, or completely prevent, Otto's reaction. *o*-Toluidine and zinc lactate inhibit Otto's reaction and render Mandelin's reaction less marked; the same is the case with quinoline and terpenes, with which Mandelin's reaction rapidly disappears, so that the usual changes of colour cannot be observed. Piperonaldehyde, lecithin, and papain do not interfere with Otto's reaction appreciably, but modify Mandelin's reaction. In large proportions, antipyrine, *o*-acetoxybenzoic acid, menthol, "analgen," apolysin (phenetidine citrate), and salicylic acid mask Otto's reaction, and with Mandelin's reagent give a transitory, bluish-green or a stable, dirty green coloration (salicylic acid). Both reactions are modified or retarded by preponderating proportions of citric or piperonylic acid, quinine, euquinine, dextrose, or mannitol.

On the other hand, the red streaks given by anilides with potassium dichromate are readily distinguished from those obtained with strychnine, and neither of the above reactions is disturbed by a large number of compounds in therapeutic use, these including caffeine, "salophene," amygdophenine (phenylglycolyl-*p*-phenetidine), theobromine, *o*-benzoicsulphinide, saligenin, sulphonal, trional, tetronal, veronal, and antithermine (lævulic acid phenylhydrazone).

In the toxicological investigation of strychnine, the latter may be separated from extraneous substances by taking advantage of its almost complete insolubility in cold water, absolute alcohol, and anhydrous ether, its very slight solubility in boiling water, its slight solubility in cold 90% alcohol, benzene, carbon tetrachloride, amyl alcohol, glycerol, light petroleum, and carbon disulphide, and its ready solubility in chloroform. T. H. P.

Analysis of Tanning Materials. I. An Improved Basic Chloride Shake Method. HUGH GARNER BENNETT (*J. Soc. Chem. Ind.*, 1914, **33**, 1182—1184).—The "basic chloride shake method" now in use as the official method for the analysis of tanning materials does not sharply distinguish between the tannin and non-tannin content of the material, a considerable proportion of non-tannin substances being absorbed by the hide powder and

reported as tannin. The author suggests that more trustworthy results would be obtained, that is, the tannin content would be lower, and the non-tannin content higher, if the method were modified as follows: (1) The hide powder to be exactly neutralised before chroming. (2) Only 5 grams of hide powder to be used for each analysis. (3) To 100 c.c. of infusion of ordinary strength, 100 c.c. of water to be added before the prepared hide powder, and the total volume to be made up to 220 c.c.; any convenient aliquot portion of the solution may be evaporated, and the residue weighed. (4) The chroming liquor to be a solution of the salt $Cr_2(OH)_4Cl_2$ instead of $Cr_2(OH)_3Cl_3$. W. P. S.

Analysis of Tanning Materials. II. Tannery Liquors. Hugh Garner Bennett (*J. Soc. Chem. Ind.*, 1914, **33**, 1184—1186).—The modified basic chloride method (see preceding abstract) is more trustworthy than the usual method when applied to the analysis of used tan liquors. The liquor is filtered, and diluted so as to contain from 0·17 to 0·23% of tannin; 50 c.c. or less of this solution are evaporated with the addition of 5 c.c. of 0·5% tartaric acid solution, and the residue is dried for one hour at 100°. The weight of the residue, less that of the added tartaric acid, gives the total solids present. One hundred c.c. of the solution are then mixed with 2·5 grams of neutralised and chromed hide powder, 12·5 c.c. of water, less the amount contained in the hide powder, are added, the mixture is shaken for fifteen minutes, filtered, and the solids estimated by evaporating 55 c.c. or less of the filtrate with the addition of tartaric acid. The result gives the quantity of non-tannins in the liquor. The hide powder is prepared for use by estimating the moisture in it, then neutralising a portion equivalent to 2·5 grams of the dry powder, after the addition of ten times its weight of water, and treating it with 0·5 c.c. of a solution obtained by dissolving 100 grams of crystallised chromic chloride and 40 grams of anhydrous sodium carbonate in 1 litre of water. The hide powder and chrome solution are shaken for one hour, the powder is then washed until free from chlorides, squeezed to contain about 70% of water, and weighed; the quantity of water remaining in the 2·5 grams of hide powder is thus ascertained. W. P. S.

Tannins of Valonia, Oakwood, and Chestnutwood. Hugh Garner Bennett (*J. Soc. Chem. Ind.*, 1914, **33**, 1186—1187).—These three tannins may be distinguished from each other by the action of bromine water on a solution of the products obtained when the solid extracts are submitted to dry distillation. The extract is heated in a test-tube provided with a delivery tube, and the distillate is received in another tube. The distillate is then shaken with 15 c.c. of water, the mixture is filtered, and the filtrate treated with an excess of bromine water. Under this treatment, valonia yields a dense, yellow, crystalline precipitate of tribromophenol bromide, m. p. 139—141° (decomp.); the precipitate should be washed with cold alcohol before the melting point is determined.

The distillate from chestnut tannin does not give a precipitate with bromine, whilst that from oakwood tannin yields a turbidity only. W. P. S.

The Catalytic Reactions of Blood. I. The Factors Involved in the Benzidine Test for Occult Blood. W. G. LYLE, L. J. CURTMAN, and J. T. W. MARSHALL (*J. Biol. Chem.*, 1914, **19**, 445—457).—The sensitiveness of the test is influenced by the relative concentrations of the reagents used—benzidine, acetic acid, and hydrogen peroxide. Under favourable conditions, occult blood can be detected when diluted one to five million times. But if inhibiting substances are present, the reagent can be made more resistant to them by increasing the strength of the benzidine, but then it fails to respond to very dilute blood. The acetic acid merely holds the benzidine in solution; excess lessens the delicacy of the test and increases the speed of fading. The peroxide supplies the necessary oxygen, and bleaches the blue colour; excess must therefore be avoided; excess further destroys the catalytic power of the blood, and, by reacting with benzidine, produces inhibitory substances. The water used should have been distilled in glass vessels. The peroxide should be added last. W. D. H.

Identification of Traces of Bilirubin in Albuminous Fluids A. A. HYMANS VAN DEN BERGH and J. J. DE LA FONTAINE SCHLUITER (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 807—810).—To detect with certainty the presence of small quantities of bilirubin in blood serum or other albuminous fluid, 20 c.c. of pure acetone are added to 10 c.c. of the serum, and the more or less intensely yellow solution, after removal of the albumin precipitate, is evaporated in a vacuum at the ordinary temperature until the acetone has been removed. The residual aqueous solution is treated with ether to remove the fatty substances, 2 c.c. of chloroform are added, and the mixture is faintly acidified with hydrochloric acid and well shaken. The chloroform solution containing the bilirubin is thoroughly washed with water to remove all the hydrochloric acid, and is dried, if necessary, with anhydrous sodium sulphate. Bilirubin can be detected in the yellow chloroform solution by the usual tests, by the reactions of Gmelin and of Ehrlich, and by the isolation of yellow, microscopic crystals.

The following remarkable observation has been made during the examination of the serum of two patients suffering from obstructive jaundice, and only in these two cases. After the blood serum had been treated by the preceding method, the final chloroform solution was allowed to evaporate slowly at 0°; when the concentration had reached a certain value the yellow colour of the solution changed suddenly to green, evidently owing to a change of bilirubin to biliverdin. C. S.

General and Physical Chemistry.

The Density of Liquid Hydrogen and the Refractive Index and Dispersion of Liquid Hydrogen and Liquid Nitrogen. HERBERT AUGUSTIN (*Ann. Physik*, 1915, [iv], **46**, 419—445).—The density of liquid hydrogen was determined by the displacement method using a cylindrical plummet of fused quartz. The mean value obtained is 0·07105 at −252·83° and 745·52 mm. The refractive indices were obtained by the method of total reflexion. The values for liquid hydrogen at −252·83° and 745·52 mm. and for liquid nitrogen at −195·83° and 745·12 mm. are recorded for several different wave-lengths, as in the following series, the numbers for nitrogen being enclosed in brackets: λ 656·3, 1·10924 (1·19715); λ 579·0, 1·10974 (1·19746); λ 546·1, 1·11003 (1·19788); λ 435·9, 1·11179 (1·20010); λ 404·7, 1·11262 (1·20125).

According to Wiener, the Lorenz-Lorentz formula for the refractivity should be written in the form $(n^2-1)/(n^2+u)d$, where u is a quantity which depends on the configuration of the molecules. By applying the formula to the data for the refractivity of hydrogen and nitrogen in the liquid and gaseous states, the value of u for hydrogen is found equal to $2{\cdot}00\pm0{\cdot}02$, and for nitrogen equal to $2{\cdot}12\pm0{\cdot}02$. The conclusion drawn from these numbers is that hydrogen behaves dielectrically as if its molecules were spherical, whilst the behaviour of nitrogen suggests that the molecules are only approximately spherical. H. M. D.

The Double Bands [in the Spectrum] of the Residual Rays of Diatomic Substances. W. C. MANDERSLOOT (*Physikal. Zeitsch.*, 1915, **16**, 36—37).—The author directs attention to the similarity in the double bands which occur in the ultra-red spectra of diatomic gases and in the residual ray spectra of diatomic solid substances such as the halogen compounds of the alkali metals and of silver. Calculation shows that the distance between the atoms is approximately the same in the two cases, but the force with which the atoms are held in position appears to be considerably greater in the case of the molecules of gases. H. M. D.

The Conditions of Emission of Certain Band Spectra of Nitrogen and Carbon. R. SEELIGER (*Physikal. Zeitsch.*, 1915, **16**, 55—59).—In a previous paper (Gehrcke and Seeliger, A., 1912, ii, 517) it has been shown that the luminosity of various gases bombarded by cathode rays changes in colour and intensity when the velocity of the cathode rays is altered. The method of experiment has now been applied to the determination of the conditions which give rise to the emission of certain banded spectra.

The results obtained show that the nitrogen bands of the second positive group are strongly excited by slow cathode rays (<20 volts), feebly by cathode rays of greater velocity, and not

at all by canal rays. On the other hand, the negative nitrogen bands are most readily excited by high-speed cathode rays, and to a smaller extent by slow cathode rays and canal rays. The bands of carbon and its compounds appear to be excited equally well by both slow and fast rays. Canal rays give rise to a feeble emission of the cyanogen and the hydrocarbon bands, and also the Swan spectrum, but the carbon monoxide bands are not excited by the positive rays. H. M. D.

A New Type of Series in the Band Spectrum Associated with Helium. A. FOWLER (*Proc. Roy. Soc.*, 1915, [*A*], **91**, 208—216).—The band spectrum described by Curtis (A., 1913, ii, 811) and Goldstein (*ibid.*, 539) has been subjected to a preliminary analysis. It is found that some of the bands have double and others single bands. The double-headed bands are not distributed according to the usual law of band spectra, but can be arranged in two series of the type hitherto exclusively associated with line spectra. Nine bands belonging to the main series of doublets have been identified, as well as four belonging to the fainter second series. Both series can be approximately represented by the usual formulæ involving the Rydberg constant.

The two series of double-headed bands are comparable with the principal and diffuse series associated with line spectra, although the usual relation between such series is not indicated with certainty, and nothing corresponding with the sharp series has as yet been identified. The doublet separations are not in accordance with those exhibited by line spectra; they diminish in passing along the series, but do not vanish at the limit.

The single-headed bands have also been examined, but no regularity in the arrangement has been recognised. H. M. D.

Displacements in Certain Spectral Lines of Zinc and Titanium. GENEVIEVE V. MORROW (*Phil. Mag.*, 1915, [vi], **29**, 394—407).—The question of the displacement of spectral lines has been studied by accurate wave-length measurements of seven lines in the arc and spark spectra of zinc and of thirteen lines in the spectra of titanium. The results obtained show that the wave-lengths are not absolutely constant, but that the lines are shifted towards the red under certain conditions. In general, the wave-lengths of the lines in the spark spectrum are greater than those in the arc spectrum, but the amount of the displacement of the different lines varies very considerably. In the arc spectrum, the displacement increases with the current, and this is attributed to an increase in the density of the vapour. The wave-lengths of the measured lines are not sensibly affected by the presence of other elements in the arc or spark, and seem to be determined by the density of the vapour of the metal under examination.

It is pointed out that over-exposure of the plates may readily give rise to errors in measurements of this kind. An apparent alteration of the wave-length may be found which is really due to unsymmetrical broadening of the silver deposit on the plate.

H. M. D.

The Spectra of Ordinary Lead and Lead of Radioactive Origin. THOMAS R. MERTON (*Proc. Roy. Soc.*, 1915, [*A*], **91**, 198—201).—A comparison has been made of the wave-lengths of some of the principal lines in the spectra of ordinary lead and of lead from Joachimsthal pitchblende. The spectra were produced in the carbon arc, the carbons being cored with the pitchblende residues or with iron oxide containing a little ordinary lead. Photographs, obtained with a concave grating spectrograph, in which the two spectra were juxtaposed, show that the lead lines are identical. From measurements of the lines between λ 3500 and λ 4100 made with a Hilger micrometer, it may be concluded that any difference in wave-length does not exceed 0·03 Å.U.

A more accurate analysis of the line λ 4058 was made by photographing the ring systems produced by a Fabry and Perot étalon. Measurements of the diameters of the interference rings agree within the limits of experimental error, and calculation shows that any difference in the wave-length of the line λ 4058 in the spectra of ordinary and radioactive lead cannot exceed 0·003 Å.U.

H. M. D.

The Spectrum of Gadolinium. E. PAULSON (*Physikal. Zeitsch.*, 1915, **16**, 7—8).—The spectrum of gadolinium contains seven groups of lines which are characterised by constant differences between the wave-numbers of corresponding members of the several groups. A similar relation has already been pointed out in reference to the palladium spectrum (this vol., ii, 34). H. M. D.

Internally Complex Salts. XIV. Light Absorption with Internally Complex Salts. H. LEY and H. HEGGE (*Ber.*, 1915, **48**, 70—85).—The absorption of the cupric salts of the amino-acids glycine, α- and β-alanines, piperidinoacetic acid, αβ-diamino-propionic acid, anilinoacetic acid, and aceturic acid has been examined in the visible and the ultra-violet spectrum.

In the visible spectrum it is found that the "leaflet" and "needle" forms of copper glycine in aqueous solution possess identical absorptive power, which is considerably influenced by the addition of ammonia. The introduction of substituents into glycine at the methylene group causes an appreciable but not radical alteration in the colour of the copper salt, but substitution at the amino-group causes a much greater effect. The introduction of a second amino-group also considerably affects the colour of the copper salt. In the red and the yellow of the visible spectrum all the above salts show a more marked absorption than copper sulphate.

In the ultra-violet region the formation of an internally complex salt from the cupric cathion and the anion of an aminoacetic acid is accompanied by a marked bathochromic effect.

The results are discussed in their bearing on the existence of subsidiary valencies in the respective molecules of the salts and the part played by these subsidiary valencies in the formation of internally complex salts. D. F. T.

The Absorption Spectrum of Chlorophyll. II. D. VAN GULIK (*Ann. Physik.*, 1915, [iv], **46**, 147—156. Compare *ibid.*, 1907, **23**, 277).—The ultra-red absorption of pure chlorophyll has been investigated in carbon disulphide solution by observations extending from $\lambda = 570\ \mu\mu$ to $\lambda = 3540\ \mu\mu$. Chlorophyll-*A* shows a strong band with a maximum at λ 650 and also a secondary band with a maximum between λ 800 and λ 900. In this region, chlorophyll-*B* shows maximum absorption at λ 630, but there is no evidence of a secondary band at λ 800—900.

Between λ 1000 and λ 3200 there are no absorption bands, but both chlorophyll-*A* and -*B* show fairly strong absorption between λ 3300 and λ 3540. In both cases the absorption curves exhibit a principal maximum at λ 3400 and a secondary maximum at λ 3500.

H. M. D.

The Constitution of the Aminoazo-compounds. EDWARD CHARLES CYRIL BALY and ROBERT ERNEST VICTOR HAMPSON (*Trans.*, 1915, **107**, 248—255).—The bluish-red colour of aminoazobenzene hydrochloride can be easily explained by attributing to it the quinonoid structure $Ph{\cdot}NH{\cdot}N{:}C_6H_4{\cdot}NH_2Cl$, and this formula appears to be supported by the yellow colour of the ammonium salt

$$Ph{\cdot}N_2{\cdot}C_6H_4{\cdot}NMe_3I$$

(compare Hewitt and Thole, T., 1910, **97**, 511). Further investigations by Hantzsch (A., 1907, i, 536) reveal considerable difficulties in the way of this simple explanation, and have led to the proposal of three possible formulæ for the constitution of the salts of aminoazobenzene, namely,

$$Ph{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NH_2,HX,\ Ph{\cdot}N_2(HX){\cdot}C_6H_4{\cdot}NH_2,\ \text{and}$$
$$Ph{\cdot}NH{\cdot}N{:}C_6H_4{:}NH_2X,$$

each of these formulæ being characterised by a different type of absorption spectrum.

The authors have re-investigated the absorption spectra of azobenzene, aminoazobenzene, dimethylaminoazobenzene, and benzeneazophenyltrimethylammonium iodide under various conditions. In preparing solutions of aminoazobenzene hydrochloride it is found sufficient to add 1% of hydrochloric acid to an alcoholic solution of the parent base when the characteristic bluish-red colour is developed. If, now, 1% of hydrochloric acid is added to an alcoholic solution of benzeneazophenyltrimethylammonium iodide the solution turns red and exhibits an absorption spectrum which is quite different from that of the parent compound when dissolved in alcohol or in concentrated sulphuric acid. Since the explanation of the colour change must be the same in each case, it seems impossible to attribute the effect to the formation of the quinonoid salt.

The authors are led to the conclusion that it is unnecessary to consider an absorption curve as characteristic of a particular primary structure. All the phenomena can be simply explained by the conception of molecular fields of force and the opening-up of these by the solvent, with the result that other light waves are absorbed. Considering the substances here dealt with, they can

all show four absorption bands, namely, about $1/\lambda = 1900$, 2300, 2600, and 3200. The nature of the solvent determines which of these different powers of absorption are called into play. The effect of the solvent depends to a certain extent on the nature of the affinity of the molecule. Each power of absorbing a definite light vibration is characteristic of the molecules of the azo-compounds dealt with, but these powers are latent, and are called into play by the use of the proper solvent. The existence of several possibilities possessed by one and the same substance of absorbing different light waves has been discussed by Baly (A., 1914, ii, 318), and it has been shown that all such absorption bands in the ultra-violet and visible regions of the spectrum are directly connected with a fundamental vibration in the infra-red, which is known to be characteristic of the substance itself, and not of any structural isomeride, and therefore the visible and ultra-violet absorption bands must also be characteristic of the substance itself, and not of any structural isomeride. An attempt to explain all such absorptive powers by different structural formulæ only leads to an impasse. H. W.

Phosphorescent Selenides of the Alkaline Earth Metals. FRITZ KITTELMANN (*Ann. Physik.*, 1915, [iv], **46**, 177—196).—In continuation of the work of Pauli (A., 1912, ii, 714), the author has prepared a further series of phosphorescent alkaline earth metal selenides, and made a comparative study of their phosphorescent properties. In all the active preparations, which contained copper, manganese, bismuth, lead, silver, zinc, nickel, or antimony as the metallic "impurity," the phosphorescent light was found to show a maximum near the red end of the spectrum. By projecting a bright spectrum on a layer of the phosphorescent sulphide, it was possible to obtain approximately the connexion between the incident radiation and the phosphorescent emission. This connexion is illustrated by a series of curves in which the approximate intensities are plotted against the wave-length. These curves show that the phosphorescent band has its maximum in all cases at a greater wave-length than that which corresponds with the exciting light.

The influence of temperature on the behaviour of the phosphorescent selenides was also examined, and the previous conclusion confirmed, namely, that the upper temperature limit, above which the selenides are inactive, is in general lower than for the corresponding sulphides.

So far as the visible spectrum is concerned, the number of phosphorescent bands exhibited by the selenide is small in comparison with that shown by the sulphides. The chief maxima are also found to be displaced towards the red end of the spectrum as compared with the maxima characteristic of the corresponding sulphides. The intensity and the duration of the phosphorescence are also much smaller for the selenides than for the sulphides. The relation between the two groups of active substances is discussed with reference to Lenard's theory. H. M. D.

Magnetic Rotatory Power of Liquefied Gases. J. CHAUDIER (*Ann. Physique*, 1914, [ix], **2**, 127—141).—The magnetic rotatory power and rotatory dispersion of liquid oxygen, nitrogen, sulphur dioxide, carbon dioxide, carbon disulphide, and methyl chloride have been investigated. From observations made with light of wave-length $\lambda = 626$, 610, 589, 578, 546, 501, and 436 $\mu\mu$, it is found that the magnetic rotation for nitrogen, sulphur dioxide, and methyl chloride varies approximately in the inverse ratio of the square of the wave-length of the light employed. The dispersion shown by carbon dioxide and carbon disulphide is much greater than that required by Biot's law, whilst oxygen diverges from this law in the opposite direction in that its rotatory dispersive power is much too small.

The following values of the magnetic rotatory power for the D line are recorded, these numbers representing the rotation produced by a column of liquid 1 cm. in length with a magnetic field strength of 1 Gauss. The temperatures of the observation are indicated in brackets. Nitrogen ($-195{\cdot}5°$), $0{\cdot}415 \times 10^{-2}$; oxygen ($-182{\cdot}5°$), $0{\cdot}782 \times 10^{-2}$; sulphur dioxide ($-10°$), $1{\cdot}8 \times 10^{-2}$; methyl chloride (18°), $1{\cdot}29 \times 10^{-2}$; carbon dioxide (26°), $0{\cdot}207 \times 10^{-2}$; carbon disulphide (18°), $4{\cdot}30 \times 10^{-2}$.

Assuming that the magnetic rotatory power remains unchanged when the substance passes from the liquid to the gaseous state, the author has calculated the rotatory power of oxygen, nitrogen, carbon dioxide, sulphur dioxide, and nitrous oxide as gases at *N.T.P.* The values thus obtained agree fairly well with those deduced from the direct measurements of Becquerel and Siertsema.

H. M. D.

Refraction and Magnetic Rotation of Acetylenic Compounds. CH. MOUREU, P. TH. MULLER and J. VARIN (*Ann. Chim.*, 1914, [ix], **2**, 269—280).—A more detailed account of work already published (compare A., 1906, ii, 1; 1913, ii, 994). W. G.

Condensation Nuclei produced by the Action of Light on Iodine Vapour. HAROLD PEALING (*Phil. Mag.*, 1915, [vi], **29**, 413—419. Compare Owen and Pealing, A., 1911, ii, 353).—A further study has been made of the formation of nuclei which occurs when light is allowed to fall on a mixture of moist air and iodine vapour. The majority of the experiments were made with moist air which had been admitted to the expansion chamber after passing through a plug of glass-wool. The most important new fact established is that the effect, after having become inappreciable, can be renewed by drawing carefully purified water over the surface of the glass-wool. This would seem to show that the formation of nuclei is not dependent on traces of foreign substances on the glass-wool or in the water. These observations furnish, therefore, further support for the view that the nuclei are formed as a result of chemical action. Of various possibilities, the balance of evidence suggests that the reaction takes place between iodine and oxygen and probably water-vapour, and that this change is catalytically influenced by the glass.

The objections put forward by Ramsauer against this view have been examined, and facts which disagree with this author's interpretation of the phenomenon are also cited. There is no evidence whatever of the formation of hydriodic acid, which should be detectable if the formation of nuclei is due to the changes $H_2O + I_2 = HI + HIO$, $HIO + O_2 = HI + O_3$, as suggested by Ramsauer. H. M. D.

Photochemical Formation of Electrolytes. MARCEL BOLL (*Ann. Physique*, 1914, [ix], **2**, 5—54, 226—268).—A comprehensive study has been made of the photochemical decomposition of the chloroplatinic acids in very dilute aqueous solution, and some observations relating to the decomposition of oxalic acid in presence of uranyl nitrate are also described.

The progress of the photochemical reactions was determined by measuring the accompanying increase in the electrical conductivity of the solution. In view of the high dilution ($v = 10{,}000$), Kohlrausch's method could not be employed, but a method of measuring high resistances has been worked out, which involves the use of an alternating current and a quadrant electrometer as null instrument, and affords accurate results even in very dilute solution.

In a preliminary series of experiments, in which the solutions were exposed to the light rays emitted by a mercury quartz lamp, it was found that the photochemical decomposition of all the chloroplatinic acids proceeds in agreement with the formula for a bimolecular reaction. In all cases the reaction is practically complete, and from the observed differences between the final and initial conductivities it would seem that two molecules of hexa-, penta-, tetra-, di- and mono-chloroplatinic acid give rise respectively to 11, 9, 7, 3, and 1 molecules of hydrochloric acid. According to these observations, the several photochemical reactions may be represented by the following general equation:

$$2H_2PtCl_n(OH)_{6-n} + (2n-1)H_2O = (2n-1)HCl + H_2PtCl(OH)_5, H_2Pt(OH)_6,$$

where $n = 6$, 5, 4, 2, or 1. The solutions, which are obtained when the photochemical decomposition has run its course, are metastable, and as a general rule deposit a reddish-brown precipitate of platinic hydroxide. This change is accompanied by a further rise in the conductivity of the solution corresponding with the liberation of another molecule of hydrochloric acid as represented by the equation $H_2PtCl(OH)_5, H_2Pt(OH)_6 + H_2O = HCl + 2H_2Pt(OH)_6$.

The fact that the above photochemical changes are bimolecular is of particular interest in view of Luther's opinion (*Zeitsch. Elektrochem.*, 1908, **14**, 450) that such reactions are always unimolecular.

Experiments with tetrachloroplatinic acid, in which the solutions were subjected to the influence of monochromatic ultra-violet light (λ 2536 and λ 2655), have shown that the reaction velocity is proportional to the intensity of the incident radiation. Absorption of the active rays takes place in accordance with the exponential

formula representing the combination of Beer's and Lambert's law. Under these circumstances, the photochemical decomposition of the chloroplatinic acids can be made use of in the construction of a chemical actinometer covering a range which extends from the yellow to the extreme ultra-violet.

From observations made with monochromatic light of wave-length varying from λ 2378 to λ 5460, it is found that the reaction velocity increases with the frequency according to an exponential formula. For light of definite wave-length, the velocity increases considerably with rise of temperature.

The chief results obtained in the investigation are summarised in the formula $V=\phi M e^{a\nu} I_0 c \,.\, (1-e^{-\chi lc})/\chi$, in which M the molecular weight of the substance, ϕ and a numbers which depend on the photochemical sensitiveness (photochemical lability), and χ the molecular absorption, are constants, in terms of which the velocity v of the reaction is represented as a function of the molecular concentration c, the thickness of the absorbing layer l, and the intensity I_0 of the incident radiation of which the frequency is ν.

The experiments relating to the photochemical decomposition of oxalic acid indicate that this reaction is unimolecular, and from the total change in the electrical conductivity the author draws the conclusion that the chemical reaction corresponds with the equation $H_2C_2O_4 + O = 2CO_2 + H_2O$. The uranyl nitrate present in the solutions acts as a catalyst. In agreement with the observed unimolecular character of the reaction, it is found that the velocity is proportional to the quantity of light absorbed by the solution, and that this proportionality is independent of the concentration of the oxalic acid.

The applicability of Bodenstein's theory (A., 1913, ii, 819) to the two reactions studied has been investigated by a series of special experiments. The results obtained show that the speed of these reactions is not appreciably affected by those agencies which are known to have an influence on the number and concentration of free electrons. The conclusion is drawn that these photochemical changes do not conform to the theory and the classification of photochemical changes which has been suggested by Bodenstein.

Finally, the experimental data have been examined from the point of view of the quantum theory. The ratio $h\nu/\epsilon$, where ϵ is the energy absorbed in the decomposition of a molecule, ν is the frequency of the incident radiation, and h Planck's constant, affords a measure of the number of molecules which are decomposed by one quantum of energy. In the case of tetrachloroplatinic acid the value of $h\nu/\epsilon$ decreases from 4·9 for light of wave-length λ 2378 to 0·004 for the wave-length λ 5460. According to Einstein's law of photochemical equivalence, $h\nu/\epsilon = 1$, but the conditions required for the realisation of this relation are by no means satisfied by the two photochemical changes which have been submitted to examination. Under these circumstances, the enormous divergences actually observed cannot be put forward as an argument against Einstein's views. H. M. D.

Chemical Actions of Light. XXXI. Autoxidations. VIII. GIACOMO CIAMICIAN and P. SILBER (*Ber.*, 1915, **48**, 181—187). —The behaviour of nicotine and piperidine in the presence of oxygen towards light has been studied.

Three 5-litre flasks, each containing 12 grams of nicotine dissolved in 100 c.c. of water and filled with oxygen, were exposed to the light from May to November. The oxygen was almost exhausted, and the product was faintly acid. The solution was diluted, mixed with barium carbonate, and distilled in steam, the bases being absorbed by hydrochloric acid. The dry hydrochlorides were then converted into the aurichlorides, which were recrystallised from water. The main bulk was nicotine aurichloride, whilst the mother liquors were freed from gold and the remaining bases identified as ammonia (by the platinichloride) and methylamine (by the aurichloride).

The non-volatile residue was filtered, evaporated in a vacuum, and the residue was extracted with absolute alcohol, which left a small quantity of the barium salt of nicotinic acid. The extract was evaporated, and the syrup (30 grams) was dissolved in about 4·5 litres of water and precipitated by the same volume of saturated picric acid solution. After allowing a resinous substance to settle, the turbid liquid was shaken, when a yellow picrate, m. p. 168°, was deposited. This is probably the picrate of oxynicotine.

Nicotine therefore suffers autoxidation, first to oxynicotine and then to nicotinic acid and methylamine, thus:

$$C_{10}H_{14}N_2 \longrightarrow C_{10}H_{14}ON_2 \longrightarrow C_5H_4N\cdot CO_2H + MeNH_2.$$

Piperidine was examined in the same way. The bulk of the base was recovered unchanged. The non-volatile bases contained, apparently, aminovaleraldehyde (platinichloride, m. p. 200°), whilst the soluble barium salts present in the same alcoholic extract were those of formic and, probably, glutaric acids. The residue of barium salts yielded formic and succinic acids. Piperidine therefore suffers auto-oxidation to a less extent than nicotine, but the degradation proceeds far.

[*Supplement.*] Pinacolin, which by itself changes into butylene and acetaldehyde (A., 1910, i, 496), was also exposed during the summer, in presence of water and oxygen. Carbon dioxide was found in the flasks. The solutions were neutralised with *N*-sodium carbonate and distilled, leaving sodium formate and acetate behind. The distillate, which contained much formaldehyde, was saturated with potassium carbonate, and the oil (17 grams from 40 grams of pinacolin) was treated with semicarbazide, which precipitated acetone semicarbazone, leaving trimethylcarbinol, b. p. 82°, m. p. 25°, in the filtrate. J. C. W.

Chemical Actions of Light. XXXII. GIACOMO CIAMICIAN and P. SILBER (*Ber.*, 1915, **48**, 187—190).—An observation that mirrors of copper or lead are deposited when vessels which contain benzaldehyde and the salts of benzoic acid are exposed to the light, has led the authors to commence a systematic study of such phenomena.

Seven tubes, each containing 6 grams of cupric benzoate, 2 grams of benzaldehyde, and 50 c.c. of benzene, were exposed from March to September. A metallic mirror was deposited, and the tubes contained a grey, crystalline powder, a small amount of a heavy, brown powder, and some well-developed blue crystals, whilst the solution itself was yellowish-brown. The solid (10 grams) was washed with benzene, and the grey crystals were removed from the brown powder (metallic copper) by means of an electrified ebonite rod. These consisted most probably of *cuprous benzoate*. The benzene mother liquor contained dissolved cuprous benzoate, for it became green in the air. The residue after evaporation contained cupric benzoate (2·9 grams), an oil (9 grams)—chiefly benzaldehyde—and benzoic acid as the main product (20 grams). The reaction belongs, therefore, to the class of simultaneous oxidation and reduction.

Cupric benzoate and acetaldehyde were also exposed to light when about 91·5% of the salt was reduced directly to metallic copper. Benzoic acid, acetic acid, and some cuprous salt were also formed. J. C. W.

The α-Radiation of Bismuth from Pitchblende. Lise Meitner (*Physikal. Zeitsch.*, 1915, **16**, 4—6).—According to experiments made by Fajans and Towara (*Naturwissenschaften*, 1914, **2**, 685), the residues from pitchblende (Joachimsthal) contain a new element of the bismuth series which emits α-rays and is characterised by a half-decay period of less than 10^8 years. For various reasons this result seemed to be improbable, and the author has re-investigated the bismuth residues from the above source. It is found that the α-ray activity exhibited by the bismuth is due to ionium, and that it can be completely removed by the addition of a small quantity of thorium to the bismuth solution, and subsequent separation of these elements by appropriate methods. H. M. D.

The Gases produced by Radioactive Substances. Decomposition of Water. A. Debierne (*Ann. Physique*, 1914, [ix], **2**, 97—127. Compare A., 1904, ii, 223, 729; 1905, ii, 623; 1909, ii, 364).—The author gives a summary of the results which have been obtained up to the present time in the investigation of the gases produced in the decomposition of water by radioactive substances. These results would seem to show that the chemical decomposition is due to the action of the α-, β-, and γ-rays which are emitted by these substances.

It is suggested that the products of decomposition are formed in three different ways: (1) by direct collision of the charged particles with the molecules of water, (2) by local rise of temperature along the path of the particles, (3) by ionisation and subsequent interaction between the ions and other constituents of the water. The ions produced by the action of the rays on water are supposed to be similar to the ions produced in gases, and are represented by the symbols H_2O^+ and H_2O^-. By interaction of these

ions with the hydrogen and hydroxyl ions in the water, hydrogen, hydrogen peroxide, and oxygen are formed in accordance with the equations: $H_2O + \overset{-}{H} = H + H_2O$; $\overset{+}{H_2O} + \overset{-}{OH} = H_2O + OH$; $2OH = H_2O_2$; $4OH = 2H_2O + O_2$.

The relative importance of the above three processes cannot be determined with any degree of certainty, but it would seem that the first and second are of greater significance for the α-rays than for the β-rays. The fact that nearly pure hydrogen is obtained in the decomposition of water by β-rays would suggest that the gaseous product is in this case due to the third process. The importance of the third process in the action of both kinds of rays is shown by a calculation of the quantity of gas which would be evolved by 1 gram of radium in radioactive equilibrium. In this it is assumed that the number of ions formed in the water is equal to the number which would be produced in a gas. The calculated rate at which gas would be liberated is of the same order as that which has been actually observed in the author's experiments. H. M. D.

The Magnetic Spectrum of the β-Rays of Radiothorium and Thorium-X. Otto von Baeyer, Otto Hahn, and Lise Meitner (*Physikal. Zeitsch.*, 1915, **16**, 6—7).—The similarity in chemical properties of the products of the thorium and actinium series is found to be accompanied by a close parallelism in the α-ray emission. On the other hand, previous observations have led to the conclusion that radiothorium does not emit β-rays, although such rays are emitted by radioactinium. A further investigation of radiothorium and thorium-X, which were deposited electrolytically on thin platinum wires, has shown that the β-rays, emitted with a velocity equal to 0·51 and 0·47 of that of light, are due to radiothorium. In a previous paper (A., 1912, ii, 409) these rays were erroneously attributed to thorium-X. H. M. D.

The Estimation of the Content of Substances containing Small Quantities of Radium by Measurement of γ-Rays. Walther Bothe (*Physikal. Zeitsch.*, 1915, **16**, 33—36).—An apparatus is described which has been designed with the object of measuring the radium content of feebly radioactive substances by observations on the γ-rays. The results obtained show that an accuracy of about 1% is obtainable when the quantity of radium present is of the order of 10^{-4} mg. per c.c. The probable error increases to $\pm 10\%$ at a concentration of the order of 10^{-5} mg. per c.c. H. M. D.

Relation between Certain X-Ray Wave-lengths and their Absorption Coefficients. W. H. Bragg (*Phil. Mag.*, 1915, [vi], **29**, 407—412).—An examination has been made of the X-ray spectra of rhodium, palladium, and silver by means of reflexion from the (111) planes of calcite. Calcite is an accurately built crystal, resembling the diamond in this respect, and affords more accurate

measurements than rock-salt, which may be compared with a badly-ruled diffraction grating giving false images or "ghosts." The spectrum consists in each case of four lines, the two of longest wave-length (α_1 and α_2) corresponding with the strong line which Moseley (A., 1914, ii, 14, 326) has found to be emitted by a large number of elements.

Further experiments were undertaken in an attempt to throw more light on the relation between wave-length and absorption. According to Barkla's observations, the *X*-rays characteristic of any element are strongly absorbed by elements of smaller atomic weight as compared with elements of greater atomic weight. It would seem from the author's experiments that the phenomenon may be expressed in a more definite form when the wave-lengths of the characteristic *X*-rays are considered. Whether strong absorption takes place or not is apparently determined by the relation between the wave-lengths of the exciting and the emitted rays. If the wave-length of the exciting ray is shorter than that of all the rays which are characteristic of the excited element, the exciting rays will be strongly absorbed. This would seem to show that the characteristic rays of an element form a system which can only be excited as a whole. H. M. D.

Salts Coloured by Cathode Rays, and the Molecular-Force Field Theory. E. C. C. Baly (*Chem. News*, 1915, **111**, 85—86).—The author points out that the existence of metastable inorganic compounds having properties similar to those of the coloured salts produced by the action of cathode rays on certain metallic salts recently described by Goldstein (Brit. Assoc. Meeting, 1914) is anticipated by his molecular-force field theory (T., 1912, **101**, 1469, 1475; 1913, **103**, 91, 2085). The condition called by Goldstein *distension*, is the existence of the force fields of the salt in a higher stage of opening up than has hitherto been recognised. The instability of the coloured salts, and their abnormal selective absorptive power are the same properties as those possessed by their organic analogues, such as the nitrophenyl ethers, nitroanthrone, etc. The opening up of a closed molecular field is closely connected with the presence of a solvent, and this agrees with the observation that the formation of the coloured metastable metallic salts is essentially a property of their solid solutions. The phosphorescence noted by Goldstein would also be expected as a deduction from the molecular-force field theory, the absorbed energy being emitted when the metastable form is exposed to daylight and returns to the normal stable form. An abnormal reactivity of these coloured salts which is anticipated by the force field theory alone remains to be proved. G. F. M.

New Methods of Obtaining Radium from Uranium Ores. E. Ebler and W. Bender (*Zeitsch. angew. Chem.*, 1915, **28**, 25—40, 41—48).—The first part of this paper gives a detailed consideration of the various uranium minerals from which radium may be extracted, and the methods hitherto used for obtaining the crude

sulphates containing radium from these minerals. After referring to the usual method of treatment of the crude sulphates with concentrated alkali hydroxide or carbonate solutions, the authors give an account of various methods they have investigated in order to obtain a more speedy concentration of the radium. These methods depend on the reduction of the crude sulphates to sulphides.

Reduction with carbon does not give very satisfactory results unless a fairly rich barium–radium sulphate is treated, but much more satisfactory results are obtained with calcium carbide or calcium hydride as reducing agents. There are certain disadvantages in the use of each of these substances alone (compare A., 1913, ii, 904), but the method is very satisfactory when a mixture of calcium carbide and calcium hydride is used, the former moderating the violent action of the latter. With fairly rich barium–radium sulphate residues 75% of the calcium hydride may be replaced by calcium carbide, but with poorer residues the percentage of calcium hydride must be increased. The reaction is started with a fuse and then goes on of its own accord. The sulphides thus produced are richer in radium than the original material, since silicious matter is unacted on. Furthermore, when they are treated with *N*-hydrochloric acid, lead sulphide is practically insoluble, the barium and radium sulphides dissolving. The further enrichment of the radium–barium chloride mixture is then carried out by fractional precipitation with hydrochloric acid (compare A., 1913, ii, 546).

The methods hitherto used for concentrating the radium in the barium–radium chloride mixture are discussed, and the authors then give an account of various methods depending on adsorption and de-adsorption. The method depending on the use of colloidal silicic acid as an adsorbent (A., 1911, ii, 957) is not very satisfactory. Manganese dioxide hydrate, precipitated either by the interaction of potassium permanganate and manganese chloride or by the action of methyl alcohol on potassium permanganate, is a satisfactory adsorbent (compare A., 1913, ii, 659), radium being more readily adsorbed than barium. The precipitation of the manganese dioxide hydrate may conveniently be brought about in the barium–radium chloride solution. By appropriate choice of the quantity of dioxide hydrate, all the radium, together with some barium, may be adsorbed. Solution of the hydrate in hydrochloric acid and fractional precipitation with hydrochloric acid will then give a richer barium–radium chloride. Preliminary to solution, however, a further concentration of the radium may be brought about by de-adsorption with the electric current (compare A., 1913, ii, 659), or by treatment with dilute hydrochloric acid, relatively more barium than radium being extracted. It is more satisfactory, however, to use salt solutions as de-adsorbing agents. When the manganese dioxide hydrate is treated with a solution of aluminium chloride, for example, the aluminium replaces relatively more barium than radium in the manganites formed by adsorption, and thus concentration of radium

takes place. Eight other salts were tried, but aluminium chloride gave the best results, a solution containing 15 grams of crystallised aluminium chloride per litre being the best to use. T. S. P.

The Question of Isotopic Elements. GEORG VON HEVESY and FRITZ PANETH (*Monatsh.*, 1915, **36**, 75—93; *Physikal. Zeitsch.*, 1914, **15**, 797—805; 1915, **16**, 45—51).—Three series of electrochemical experiments were carried out to decide whether isotopic elements can completely replace one another chemically. The decomposition potentials of radium-*E*, and of thorium-*B* peroxide, in absence of isotopic elements, were found to be $-0{\cdot}24$ and $+1{\cdot}13$ *V.* respectively, measured against the calomel electrode. Addition to the radium-*E* solution of the isotopic element bismuth, so as to increase the concentration from about 10^{-9} *N.* to 10^{-4} *N.*, changed the decomposition potential to $-0{\cdot}14$ *V.*, which is in the direction and to the extent to be expected from Nernst's theory, if the radium-*E* and bismuth ions are electrochemically identical. For thorium-*B* addition of the isotopic element lead, to increase the concentration from 10^{-12} *N.* to 10^{-3} *N.*, changed the potential at which the peroxide is deposited to $+0{\cdot}87$ *V.*, which is again in accordance with that theory.

The deposition of minimal quantities of the above radio-elements is prevented by the presence of isotopic elements, namely, bismuth and lead respectively, but other ions, for example, thallium, are without effect.

A quantity of pure radium-*D*, estimated at some thousandths of a milligram, was prepared from radium emanation and electrolytically deposited as peroxide on a platinum wire as a visible and electrochemically active film. The *E.M.F.* of a chain consisting of this electrode in radium-*D* nitrate solution against the normal calomel electrode was the same as when the radium-*D* peroxide electrode was exchanged for a similar one of lead peroxide. The addition to the radium-*D* nitrate solution of lead nitrate changed the potential in the sense and to the extent required by Nernst's theory, showing that in this theory it is the sum of the concentrations of isotopic elements which determines the potential.

F. S.

The Electro-chemistry of Polonium. GEORG VON HEVESY and FRITZ PANETH (*Monatsh.*, 1915, **36**, 45—49).—It has been found, for the radio-elements, radium-*E* and thorium-*B*, at infinitesimal concentrations, that the decomposition potentials agree with those calculated from Nernst's formula, from the value found in normal solutions of the isotopic elements, bismuth and lead respectively. The decomposition potential of polonium in $10^{-8}N$-solution, $10^{-1}N$. with respect to nitric acid, was studied, using electrodes of gold. The latter metal was chosen as having no special affinity for polonium, which is deposited, from vapour, preferentially on platinum and palladium. Nitric acid removes all but $\frac{1}{2}$% of the polonium electrochemically deposited on gold, but leaves 13% in the case of platinum. Under similar conditions the ratio

of the amounts of polonium deposited on gold and platinum electrodes are as 2 : 3.

The polonium solution used was estimated to be $10^{-8}N$. By gradually increasing the current strength the cathode and anode potentials were gradually raised. A sudden increase in the amount of polonium deposited on the electrodes occurred at the cathode at $E_{Hg}=0{\cdot}35$ *V.*, and on the anode at $E_{Hg}=1{\cdot}05V$. The anodic deposition is to be explained, as with manganese and lead, as being due to the deposition of a peroxide of polonium. Diffusion experiments show that polonium is bivalent, and the normal potential of polonium, calculated from the decomposition potential at $10^{-8}N$., is $0{\cdot}35+8\times0{\cdot}028=0{\cdot}57$ *V.* This lies near the normal potential of silver. The calculated normal potential of polonium peroxide, in $10^{-3}N$-nitric acid, is $+0{\cdot}89$ *V.*, that of lead being 0·82 *V.* By varying the conditions it is possible to confine the deposition of polonium to the anode or cathode at will, and the fractional deposition of polonium as peroxide can be used to separate it from metals, such as gold, mercury, etc., which are not anodically deposited. Owing to the tendency to form colloidal solutions, neutral or weak acid solutions are to be avoided, $10^{-1}N$-nitric acid being suitable. F. S.

The Condensation of Thorium and Radium Emanations. Alexander Fleck (*Phil. Mag.*, 1915, [vi]. **29**, 337—361).—Experiments have been made on the condensation of thorium and radium emanations alone and mixed under a great variety of conditions, with the view of obtaining evidence whether these emanations can be separated from one another by condensation, or whether, as might on certain grounds be expected of two isotopic elements, they are inseparable by such means. In the first experiments the mixed emanations were passed through a copper spiral at various definite temperatures, and the proportion of the two emanations condensing was determined. Thorium emanation appeared at all temperatures to be the more easily condensed, but this effect is to be expected, even were the two emanations physically identical, for owing to the longer life of the radium emanation and the nature of the experiment, a part of it would revolatilise after condensation. Various experiments were made with the emanations contained in highly exhausted sealed glass tubes, in which the instantaneous diffusion of the emanation throughout the tube was proved to take place. For radium emanation evidence of two maxima, on the curve connecting the temperature and the fraction condensed, was obtained, one at $-72{\cdot}5°$ and the other at $-161°$. But different tubes showed different condensation curves, and in one case during the decay of the emanation it was found that the condensation curve suddenly entirely changed in character. As the concentration of the radium emanation diminished by decay it became more easily condensed. During an attempt to determine the curves for both emanations mixed, it was found that the amounts of both emanations condensed at liquid air temperature, making all corrections for the decay of the radium emanation,

progressively diminished as the latter decayed, and both emanations were affected to the same extent. In a repetition of the experiment this effect did not occur. Correcting for it, the result was that at every temperature the fraction of radium emanation condensed was greater than that of the thorium emanation. A discussion of the theory of the experiment shows that this effect would occur even with physically identical emanations provided the average time spent by the thorium emanation atom in the gaseous phase, between successive condensations, was comparable to its period of average life. The question could not be definitely answered owing to the way in which the condensation curves were found to vary from experiment to experiment, and even during the course of the measurements with a single tube. F. S.

The Production of Helium by Radioactive Substances. A. DEBIERNE (*Ann. Physique*, 1914, [ix], **2**, 428—488).—A more detailed account of work already published (compare A., 1904, ii, 223, 729, 642; 1905, ii, 623; 1906, ii, 257, 414; 1909, ii, 364, 534; 1910, ii, 251). W. G.

The Analysis of Gases after Passage of Electric Discharge. A. C. G. EGERTON (*Proc. Roy. Soc.*, 1915, [*A*], **91**, 180—189).—According to the experiments of Collie and Patterson (T., 1913, **103**, 419; P., 1913, **29**, 217; compare also A., 1914, ii, 847), small quantities of helium and neon can sometimes be detected in the gas pumped out from a discharge tube containing originally pure hydrogen through which an electric discharge has been passed. In a further investigation of the phenomenon by Strutt (A., 1914, ii, 201) and by Merton (A., 1914, ii, 726), negative results were obtained in all experiments in which air leakage was rigidly excluded.

In view of these divergent results, new experiments have been undertaken by the author in which special attention was paid to (1) the electrical conditions of the discharge, (2) the sensitiveness of the method of analysis, (3) the possibility of preventing access of air into the apparatus during the discharge and subsequent analysis, and of freeing completely the electrodes from all detectable traces of rare gases.

The experiments were made with a specially designed form of apparatus in which the gases from the discharge tube could be transferred directly and completely to the analysing burette without coming into contact with mercury which has an air-contact surface. The hydrogen was generated from palladium, and the oxygen employed in the analysis from potassium permanganate, the tubes containing these substances forming part of the enclosed apparatus. A charcoal bulb and a phosphorus tube, both very small, were used for the absorption of residual gases.

As the result of numerous experiments, in which electric discharge was passed with three different sized coils, three different types of interrupters, through tubes of various shapes and sizes, with palladium, platinum, and aluminium electrodes of varying size and shape, the analyses of the residual gases being carried

out in various ways, it has been found that no change takes place in the gas as a consequence of the discharge. No helium or neon is formed, as would be suggested by the experiments of Collie and Patterson.

In a theoretical discussion of the mechanism by which hydrogen might conceivably be converted into helium, it is shown that the rate of formation of helium according to the observations of Collie and Patterson is incomparably greater than that calculated on the assumption (1) that the helium is produced by a collision of four hydrogen atoms, or (2) by the action of an electron on two colliding hydrogen molecules. In this connexion it is further pointed out that the energy of cathode particles is of the order 10^{-9} erg, whilst, according to the theory of relativity, the absorption of energy required for the transformation of four atoms of hydrogen into an atom of helium amounts to 6×10^{-5} erg. Many cathode particles would therefore have to act simultaneously, or it must be assumed that their effects are additive; this would increase enormously the time required to produce a detectable quantity of helium.

On the other hand, it is possible that a partial disintegration of other atoms, such as are contained in the electrodes and the glass of the discharge tube, accompanied by the liberation of helium atoms, may be brought about under the conditions of electric stress which occur in discharge tubes, although the energy of the carriers of the electric charge is certainly not sufficient to bring about complete disintegration into helium atoms.

H. M. D.

Experiments on Ionised Gases. Ed. Salles (*Ann. Physique*, 1914, [ix], **2**, 273—346).—The author has measured the coefficients of diffusion of the positive and negative ions in various gases by Townsend's method. The special form of the apparatus used has permitted of the extension of the measurements to pressures above that of the atmosphere. Data are recorded for air, oxygen, nitrogen, and carbon dioxide at 760 mm., and for air and nitrogen at higher pressures. In general, the product of the diffusion coefficient and the pressure of the gas is constant, although the results obtained with the negative ion in nitrogen at the highest pressure investigated (1300 mm.) show that the product is greater at this pressure than at lower pressures.

Experiments made with metal tubes of steel, brass, and German silver show that the nature of the wall of the tube is without appreciable influence on the coefficient of diffusion of the ions.

In a second series of experiments, the author has measured the ratio of the mobility of the ions (k) to the coefficient of diffusion (D). The method which gives this ratio has been devised by Langevin, and depends on the determination of the saturation curves when the gases are under the influence of the ionising agent. The values obtained for k/D approximate in general very closely to the values calculated on the assumption that the positive and negative ions carry the same charge. When the gas is ionised by

the γ-rays of radium or by a small number of very penetrating β-rays, the correspondence between the observed and calculated values is so close as to warrant the conclusion that the gas ionised by these agencies contains no ions which carry more than one charge. H. M. D.

The Ionisation of Metals by Cathode Rays. NORMAN CAMPBELL (*Phil. Mag.*, 1915, [vi], **29**, 369—383. Compare A., 1914, ii, 701).—The experiments previously described for platinum have been extended to other metals and to cathode rays of higher speeds. The changes in the ionisation, which occur when platinum is heated, can be produced much more rapidly and completely in platinum, copper, and nickel by making the metal one electrode of an electric discharge in air, oxygen, hydrogen, or petroleum vapour at 2 mm. pressure. The changes are greatest in copper, and are scarcely appreciable in aluminium, and are closely connected with the amount of "spluttering" of the electrode. It appears that there are two states, "*A*" and "*B*," of a metal, which can always be reproduced. State *A* corresponds with a surface polished by emery or heated in a flame, and in it the ionisations of platinum, copper, and nickel are nearly the same. State *B* is produced by reducing the ionisation by the discharge, and restoring it by bombardment with cathode rays in a high vacuum, and in it the ionisation varies notably for different metals, and is smaller than in state *A*. The former conclusion that state *A* could be reproduced by cathode-ray bombardment is incorrect. It is suggested that state *A* differs from the other states produced by the discharge in that the metal is covered in this state with a layer of gas. For state *A* the speed of the electrons liberated from the metal does not vary with the metal or with the speed of the incident rays. For the other states no certain conclusions can be drawn. F. S.

Transmutation of the Chemical Elements. I. W. P. JORISSEN and J. A. VOLLGRAFF (*Zeitsch. physikal. Chem.*, 1914, **89**, 151—154).—Small quantities of uranium oxide were subjected to cathode rays for periods of one and two hours under a pressure of from 0·012 mm. to 0·054 mm., and the product compared with untreated uranium oxide by means of an electroscope. The results show that there is a loss of oxygen corresponding with the change of 35% of the U_3O_8 into UO_2, but there is no evidence that the uranium compound has become more active. J. F. S.

Influence of Pressure on the Electrical Conductivity of Pure Metals according to Grüneisen's Theory. BENGT BECKMAN (*Physikal. Zeitsch.*, 1915, **16**, 59—62).—The influence of pressure on the electrical conductivity of zinc, iron, and palladium has been examined for pressures up to about 2100 atmospheres. The change in the resistance (d) is accurately represented by a quadratic equation, $d = ap + bp^2$, in which p is the pressure and a and b are constants. On comparing the results obtained for these and other

metals previously investigated with the requirements of Grüneisen's theory (compare A., 1913, ii, 377), it is found that the observed change in the conductivity with pressure is of the calculated order of magnitude except in the case of bismuth and mercury. For gold, silver, aluminium, and copper the agreement is within the limits of experimental error, but for the other metals the theoretical relation can only be considered as approximate.

H. M. D.

Electrical Conductivity of Pure Liquids. J. Carvallo (*Ann. Physique*, 1914, [ix], **1**, 171—225; **2**, 142—225).—The question as to whether liquids other than water are characterised by a definite limiting conductivity in the pure state has been investigated by experiments on sulphur dioxide, ethyl ether, ammonia, acetone, methyl alcohol, ethyl alcohol, hydrogen cyanide, and hydrogen iodide. Preliminary purification was effected by a series of fractional distillations at the ordinary pressure or in a vacuum, and in some cases further purification resulted on the prolonged passage of a continuous current through the liquid. The electrical treatment was always found to be accompanied by a diminution of the conducting power in the case of ethyl ether, aliphatic hydrocarbons, and ammonia; ethyl alcohol gave an increase, methyl alcohol no effect, and with sulphur dioxide and acetone the change was variable, and depended on the sample of liquid subjected to the action of the current.

In the limiting condition reached in the case of sulphur dioxide, ammonia, ethyl ether, and the hydrocarbons, the behaviour of the liquids resembles that which is met with in gases, and suggests that these substances have no measurable characteristic conductivity in the pure state. The observations made with acetone, ethyl alcohol, and methyl alcohol do not permit of any definite statement in regard to the existence of a limiting value of the conductivity. The following values, representing the minimum observed conductivities, are recorded; in most cases these are very much smaller than the values recorded by previous observers: sulphur dioxide (15°), $1{\cdot}8\times10^{-11}$; ammonia (15°), $3{\cdot}8\times10^{-10}$, (−80°) $4{\cdot}9\times10^{-10}$; ethyl ether (16°), $7{\cdot}6\times10^{-16}$; acetone (15°), $1{\cdot}2\times10^{-10}$; ethyl alcohol (17°), $0{\cdot}9\times10^{-8}$; methyl alcohol (0—20°), $8{\cdot}0\times10^{-7}$; hydrogen cyanide (0°), $1{\cdot}1\times10^{-7}$.

From the observations it would appear that a limiting conductivity, which is independent of the intensity of the electric field, cannot be regarded as a criterion of a perfectly pure liquid, as suggested by Warburg. This independence has been found in liquids which were known to contain traces of impurities.

Under the influence of light, sulphur dioxide decomposes in accordance with the equation $3SO_2=S+2SO_3$. The impurities which are thus introduced can only be removed by distillation in a vacuum in the dark or by the electrical method. The solutions of sulphur and sulphur trioxide are photo-electrically sensitive, but the nature of this phenomenon has not been disclosed by the observations.

H. M. D.

The Influence of Soaps of the Naphthenic Acids and of Phenols on the Electrical Conductivity of Heavy Hydrocarbon Oils. D. HOLDE (*Ber.*, 1915, **48**, 14—19, 288).—It is found that the addition of calcium soaps of the naphthenic acids very considerably raises the electrical conductivity of the heavy petroleum hydrocarbons, but that a corresponding amount of the free naphthenic acids produces only a slight effect.

The presence of phenols likewise increases the conductivity of heavy tar oils, but as is the usual relation between the paraffin and benzene hydrocarbons, heavy tar oil free from phenols has a higher conductive power than heavy mineral oil. D. F. T.

The Influence of some Glycols on the Electrical Conductivity of Boric Acid. J. BÖESEKEN [with A. N. EGGINK, W. H. JAGERINK, A. KOREVAAR, F. H. LÜTTER, R. PRIESTER, and N. H. SIEWERTS VAN REESMA] (*Rec. trav. chim.*, 1915, **34**. 96—113. Compare A., 1912, i, 742; Boëseken and van Rossem, A., 1912, ii, 147).—Determinations of the effect of polyhydric alcohols on the conductivity of boric acid (*loc. cit.*) have been extended to a number of glycols, namely, α-monochlorohydrin, divinyl glycol, pinacone, propane-αγ-diol, *n*-butane-αδ-diol, α-phenoxypropane-βγ-diol, β-nitro-αγδ-trihydroxybutane, and sorbitol. The results obtained bear out the conclusions already drawn from the previous work.

In order to clear up the confusion existing as to the constitution of the products obtained by the action of sodium phenoxide on epichlorohydrin (compare Lindemann, A., 1891, 1198; Boyd and Marle, T., 1908, **93**, 838), the author has determined the physical constants of these phenyl derivatives, and examined their behaviour towards bromine. Phenyl glycide has $D_4^{21\cdot2}$ 1·1109; n_D^{21} 1·53072. Glycerol diphenyl ether, $OPh\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OPh$, has m. p. 81°, D_4^{24} 1·179, and glycerol monophenyl ether, m. p. 69°, D_4^{20} 1·225. On bromination, phenylglycide gave p-*bromophenylglycide*,

$$C_6H_4Br\cdot O\cdot CH_2\cdot CH\text{–}CH_2$$
$$\qquad\qquad\quad \diagdown\ \diagup$$
$$\qquad\qquad\quad\ O$$

a colourless liquid, b. p. 183—185°/25 mm.; $n_D^{18\cdot5}$ 1·57509; D_4^{18} 1·5743; glycerol diphenyl ether gave a *di*-p-*bromo*-derivative,

$$OH\cdot CH(CH_2\cdot O\cdot C_6H_4Br)_2,$$

m. p. 81·5°; and glycerol phenyl etner gave a p-*bromo*-derivative, m. p. 90·5°. W. G.

Conductivity of Acids in Absolute and Aqueous Alcohol. I. HEINRICH GOLDSCHMIDT [with JENS SCHJERVE and MAX E. FEIGL] (*Zeitsch. physikal. Chem.*, 1914, **89**, 129—144; *Zeitsch. Elektrochem.*, 1914, **20**, 473).—The electrical conductivity of hydrochloric acid, sulphosalicylic acid (1:2:4), sodium chloride, lithium chloride, sodium sulphosalicylate, piperidine hydrochloride, and piperidine sulphosalicylate have been determined at a series of concentrations in absolute alcohol solution and in solutions in alcohol containing known quantities of water. The following values of the equivalent conductivity at infinite dilution for absolute alcohol solutions at 25° have been obtained: Hydrochloric acid, $\lambda_\infty = 89$; lithium chloride, $\lambda_\infty = 39{\cdot}4$; sulphosalicylic acid, $\lambda_\infty = 83$; sodium chloride,

λ_∞ =46·5; piperidine hydrochloride, λ_∞ =53; sodium sulphosalicylate, λ_∞ =40·9; and piperidine sulphosalicylate, λ_∞ =48. On adding water to the alcohol solutions it is shown that the value of λ_∞ decreases rapidly at first, and then more slowly until the water is present in sufficient quantity to make a 2*N*-solution, after which it increases. The equilibrium constant of the system, hydrogen ion, water, alcohol, has been determined, and found to be 0·0583. The complex ion $H_2O{\cdot}H^{\cdot}$ migrates very much more slowly than the free hydrogen ion in alcohol solution, the difference in the ionic conductivities being expressed as 42·7. Sulphosalicylic acid behaves in an analogous manner to hydrochloric acid. Its conductivity in alcohol is affected in much the same way as hydrochloric acid by the addition of water. J. F. S.

Influence of Electrolytes on the Potential Difference at the Oil-Water Boundary of an Oil Emulsion, and at the Water-Glass Boundary. FRANK POWIS (*Zeitsch. physikal. Chem.*, 1914, **89**, 91—110).—The potential difference, existing at the boundary of oil and water in a freshly prepared oil emulsion, to which varying amounts of potassium chloride, barium chloride, aluminium chloride, thorium chloride, or potassium ferrocyanide have been added, is determined by a slightly modified form of the apparatus employed by Ellis (A., 1913, ii, 13, 1036). It is shown that the potential difference on the surface of oil drops suspended in water is approximately −0·046 volt. The addition of small quantities, up to 2·5 millimol. per litre, of potassium chloride increases the negative value, whilst larger quantities decrease it. All anions in an aqueous suspension have the tendency to make the potential difference negative, whereas cations tend to make it positive. In pure water and at small concentrations the negative influence is the greater. The influence of both cations and anions increases considerably with their valency, as is shown by the fact that the quantity of potassium chloride, barium chloride, aluminium chloride, and thorium chloride required to make the potential difference equal to zero, decreases in the order named. The positive potential brought into existence by the addition of a sufficient quantity of aluminium chloride or thorium chloride depends not on the presence of colloidal hydroxides, as has been hitherto accepted, but on the strong positive action of the $Al^{\cdot\cdot\cdot}$ ion and the $Th^{\cdot\cdot\cdot\cdot}$ ion. The influence of the above-mentioned electrolytes on the glass–water potential is much the same as in the case of the oil-water potential, except that the addition of small quantities of potassium chloride and potassium ferrocyanide does not increase the negative value of the water value. The smaller the concentration of the oil particles, the smaller the concentration of an electrolyte required to bring about a given potential difference.

J. F. S.

Influence of Time on the Potential Difference at the Surface of Oil Particles suspended in Water. FRANK POWIS (*Zeitsch. physikal. Chem.*, 1914, **89** 179—185. Compare preceding abstract).—The present paper deals with the change in the potential difference

at the boundary of oil emulsions to which varying quantities of electrolytes have been added. The method of measurement is the same as that described in the previous paper (*loc. cit.*). It is shown that the contact potential changes instantaneously or almost instantaneously on the addition of an electrolyte to an oil emulsion. The value of the potential obtained depends on the concentration of the electrolyte added. A further slow change follows the initial sudden change, which after a prolonged period reaches an equilibrium value. The slow change is shown to be due to a second cause, and not a continuation of the initial rapid change. In the presence of a stable electrolyte, such as barium chloride, the slow change leads to a value that would have been set up initially by an electrolyte of greater concentration than that present. Substances like aluminium chloride, however, act in the opposite sense, since a final value is obtained which corresponds with the initial value of a smaller concentration of added electrolyte. This is due to the increasing replacement of the aluminium ion by hydroxide due to hydrolysis. J. F. S.

Relationship between the Stability of an Oil Emulsion and the Potential Difference at the Oil–Water Surface, and the Coagulation of Colloidal Suspensions. FRANK POWIS (*Zeitsch. physikal. Chem.*, 1914, **89**, 186—212. Compare preceding abstracts).—Potential and turbidity measurements have been carried out with oil-water emulsions to which varying small quantities of potassium chloride, barium chloride, aluminium chloride, and thorium chloride have been added. The experimental method and details are the same as those previously published (*loc. cit.*). It is shown that when the potential difference at the surface of oil particles, suspended in water, reaches a definite critical value, which lies at approximately $\pm 0{\cdot}030$ volt, the emulsion is relatively stable. Should the potential difference be smaller, coagulation follows, with a velocity which is approximately the same for all values of the potential. This behaviour is not in keeping with the view that the stability decreases continuously with the potential, and at the isoelectric point is very small. The relative concentrations of thorium chloride, aluminium chloride, barium chloride, and potassium chloride necessary to produce a potential of $-0{\cdot}030$ volt are much nearer those required to bring about a rapid coagulation than those necessary to make the potential zero. When coagulation occurs, the particles do not all runt together, but collect in a number of groups. The theory of a critical potential, above which a colloidal solution is stable and below which unstable, is in accord with the larger number of known facts, and explains many facts which are not in keeping with the theory of the isoelectric point. J. F. S.

Oil Emulsions. III. Coagulation by Colloidal Solutions. RIDSDALE ELLIS (*Zeitsch. physikal. Chem.*, 1914, **89**, 145—150. Compare A., 1912, ii, 13, 1036).—Biltz has shown (A., 1904, ii, 324) that when two colloids possessing opposite charges are brought into contact there is a mutual coagulation between certain limits,

outside of which no coagulation occurs. Billiter has qualitatively established the relationship between these limits and the charge on the particles (A., 1905, ii, 305). In the present paper the connexion between the limits of coagulation and the potential difference is quantitatively determined for oil emulsions and ferric hydroxide sol. The method consists in adding colloidal ferric hydroxide drop by drop to 10 c.c. of warm oil emulsion until coagulation sets in, and by adding oil emulsion in the same way to 5 c.c. of colloidal ferric hydroxide solution. These measurements established the limits of coagulation. They were controlled by allowing the mixtures to remain for two or three days, and in those cases where coagulation had occurred, its amount was determined by filtering and comparing the amount of oil still in suspension with a known suspension, using the nephelometric method previously described (*loc. cit.*). The oil–water contact potential was determined in the various cases by the microscopic method (*loc. cit.*). It is shown that complete coagulation occurs when the potential lies between $-0{\cdot}045$ volt and $+0{\cdot}03$. A theory is put forward which offers an explanation of the results. J. F. S.

Reproducibility of the Copper Electrode. F. H. Getman (*Trans. Amer. Electrochem. Soc.*, 1914, **26**, 67—78).—The only constant and reproducible copper electrode is that composed of spongy copper. Such electrodes are prepared by electrolysing a 3·75% solution of copper sulphate, using a current density of 2·1 amperes per cm.^{2}, depositing the reddish-brown sponge on platinum wire, and washing successively with water, alcohol, and ether. Such spongy material is free from superficial strain, and is to be regarded as the stable modification of copper under ordinary laboratory conditions, whilst drawn, polished, hammered or annealed wires and dense electrolytic deposits are regarded as metastable (compare Lewis and Lacey, A., 1914, ii, 521; Cohen and Heldermann, *ibid.*, 205, 654). C. H. D.

Formation of Badly Conducting Films on Copper Anodes in Cyanide Solutions. W. Lash Miller (*Trans. Amer. Electrochem. Soc.*, 1914, **26**, 63—66).—Copper anodes in cyanide solutions become coaed with a yellowish-green deposit when high current densities are used, and the resistance rises rapidly. The effect is diminished by the addition of either cyanide or ammonia. C. H. D.

An Electrostatic Basis for the Law of Mass Action in Electrolytic Solutions. R. T. Lattey (*Chem. News*, 1915, **111**, 135—136).—The author claims that the mass action equation follows from an argument in which it is supposed that the electrostatic forces acting between the ions of an electrolyte are counterbalanced by osmotic forces. H. M. D.

The Assumption of "Double Complexes" Applied to the Salts of Copper, Silver, Cadmium, Bismuth and Iron in Opposition to Kahlenberg's Criticisms of the Ionic Theory. C. Blomberg (*Chem. Weekblad*, 1915, **12**, 242—247).—A theoretical

paper, in which the author advances arguments to prove that the facts cited by Kahlenberg as opposed to the ionic theory can be explained by the assumption of the formation of ionic complexes.

A. J. W.

Cause of the Change in the Value of the Irrationality Constant (van't Hoff's Factor *i*) for Aqueous Solutions of Sodium, Potassium, Magnesium, and Calcium Chlorides as Calculated for 0° and 100° by the Electrical and Dynamical Methods. C. H. Sluiter (*Chem. Weekblad*, 1915, **12**, 178—208).—The difference between the value of *i* calculated from the ionisation and that of *i'* calculated from dynamic measurements for certain metallic chlorides can be explained by assuming:

(1) An increase in the hydration of the salts in the order KCl, NaCl, $CaCl_2$, $MgCl_2$.

(2) An increase in hydration by falling temperature.

(3) A departure from the ideal gas laws for osmotic pressure, and therefore from Raoult's laws for the depression of the freezing point and the elevation of the boiling point of solutions.

A. J. W.

The Magnetisability of the Oxides of Manganese, Chromium, Uranium, Molybdenum, and Tungsten. E. Wedekind and C. Horst (*Ber.*, 1915, **48**, 105—112. Compare Wedekind and Hausknecht, A., 1914, ii, 25).—The magnetisability of the oxides of manganese is very similar to that of the oxides of vanadium or titanium; the monoxide is rather more strongly magnetic than the dioxide, whilst the results obtained with barium manganate and potassium permanganate show that the susceptibility decreases with increasing valency. The mixed oxide, Mn_3O_4, is most strongly magnetic, corresponding with Fe_3O_4 and Ti_3O_5, whilst the sesquioxide appears to be unexpectedly less magnetic than the other oxides.

Chromium trioxide is less magnetic than the sesquioxide, whilst the salt-like oxides, Cr_5O_9 and Cr_4O_9, are about three thousand times more strongly magnetic than the former. In the cases of the sulphides, CrS and Cr_2S_3, the susceptibility decreases with increasing valency, thus differing from the sulphides of vanadium; the greatest susceptibility is shown by the sulphide, Cr_3S_4.

Uranium di- and tri-oxides are more strongly magnetic than the metal, and show a perceptible increase in susceptibility with diminishing valency; in the case of the mixed oxide, U_3O_8, the expected increase in magnetisability is not observed. Similar results are obtained with the oxides of molybdenum and tungsten. It therefore appears that the latent magnetism of chromium is connected with its position in the horizontal series of the periodic system; neighbouring elements in the vertical series scarcely show analogies in this direction.

Barium manganate is prepared in a slightly impure state by addition of excess of aqueous barium hydroxide to a moderately concentrated solution of potassium permanganate and cautious

addition of hydrogen peroxide until the solution is only faintly pink; the dark precipitate is repeatedly washed with water.

Chromous sulphide, CrS, gray powder, D^{14} 3·909, is obtained by heating the sesquisulphide in a stream of hydrogen for twelve hours at as high a temperature as possible. The sulphide, Cr_3S_4, black powder, D^{14} 3·538, is prepared by heating a mixture of chromium sulphide and sulphur in a current of hydrogen sulphide, the temperature being gradually raised to redness. Excess of sulphur is subsequently removed by carbon disulphide. H. W.

Significance of the Dependence between Magnetic Susceptibility and Dissociation. Association between Ions and Solvent. A. Quartaroli (*Gazzetta*, 1915, **45**, i, 153—160).—It has been observed that the atomic susceptibility of iron and of manganese, in solutions of their salts, increases with the dilution, and the author found a similar increase with solutions of ferric chloride to which hydrochloric acid had been added in order to prevent hydrolysis (see this vol., ii, 157). There appears, indeed, to be a well-defined relation between magnetic susceptibility and electrolytic dissociation. The action of a magnetic field on a magnetic disperse system is discussed for the cases in which the disperse phase consists of: (1) macroscopic granules, (2) microscopic and ultramicroscopic granules, (3) amicrons and non-dissociated molecules, and (4) ions. If the solution is placed between the poles of a powerful electromagnet, then, in case (1) the granules will be attracted, and will move through the liquid towards the poles; when a little potassium sulphate is added to a moderately dilute ferric chloride solution, the granules of ferric hydroxide formed will not at first be attracted, but when they have increased sufficiently in size, a slight attraction will be observable. In colloidal solutions of magnetic substances no measurable variation occurs in the different parts of the liquid, and this behaviour is explained, on the basis of Stokes's law, as a result of the smallness of the particles. The same reasoning applies with greater force in the case of amicrons and undissociated molecules. With ions, also, no variation in the concentration takes place under the influence of the field, but the whole of the liquid undergoes either attraction to the poles or, with dilute solutions, less repulsion than is exerted on the solvent alone. In this case, then, the ions behave as though rigidly connected with the solvent, and in view of the relation between susceptibility and dissociation the conclusion is drawn that the ions and the water are bound together by electrostatic attraction. These results are discussed in their relation to Ciamician's hypothesis concerning the state of solutions of electrolytes. T. H. P.

Thermomagnetic Properties of Various Compounds at Low Temperatures. Torajirô Ishiwara (*Sci. Rep. Tôhoku Imp. Univ.*, 1914, **3**, 303—319).—The influence of temperature on the magnetic susceptibility has been investigated for a large number of substances at temperatures ranging from the ordinary to that of liquid air.

The susceptibilities of the diamagnetic substances examined are not appreciably influenced by change of temperature if there is no change in the state of aggregation. The data for ethyl alcohol, methyl alcohol, water, ethyl acetate, benzene, and toluene show a distinct change, however, at the respective melting points.

The paramagnetic substances, all of which are inorganic compounds, may be divided into two groups. For those in the first group ($KMnO_4$, CuO, $CuBr_2$, FeF_3,$3H_2O$) the susceptibility varies very slightly with the temperature. Of twenty-three compounds belonging to the second group, the variation of the susceptibility of five [$FeCl_3$, $FeCl_2$,$4H_2O$, $FeSO_4$,$7H_2O$, $Cr_2(SO_4)_3$, and $Co(C_5H_7O_2)_3$ cobaltic acetylacetonate] agrees approximately with that required by Curie's law. For twelve others the change in susceptibility satisfies the relation $\chi(T+\Delta)=$constant, in which Δ is a positive or negative constant. Whether these relations will hold at higher temperatures is to be examined in a further series of experiments. H. M. D.

Influence of the Hydration and of the Deviations from the Ideal Gas Laws in Aqueous Solutions of Salts on the Solidifying and the Boiling Points. C. H. Sluiter (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1036—1046).—Measurements have been made of the freezing point, boiling point, and the electrical conductivity at 0° and 100° of aqueous solutions of sodium, potassium, magnesium, and calcium chlorides over the range $v=1$ to $v=2000$. A comparison is made of the coefficient i' obtained from the freezing-point or boiling-point data and i derived from the conductivity measurements at 0° and 100° respectively.

At 0°, i' is always greater than i, and the difference between the two values increases with the concentration in the case of sodium, calcium, and magnesium chlorides. At a fixed concentration, the value of $i'-i$ increases in the order—sodium, calcium, magnesium. For potassium chloride, on the other hand, $i'-i$ has approximately the same value at all concentrations.

At 100°, $i'-i$ has, at certain concentrations, a negative value for all the salts examined, and in general this negative value is found in the more dilute solutions. For all the salts, at the highest concentration investigated, $i'-i$ has a positive value, and its magnitude increases in the order—potassium, sodium, calcium, magnesium.

The results are interpreted on the assumption that the deviations of the coefficients i' and i are determined partly by hydration and partly by the magnitudes of the constants a and b in the van der Waals' equation which is supposed to be applicable to the dissolved salt. H. M. D.

Isothermals of Diatomic Substances and their Binary Mixtures. XV. Vapour Pressures of Oxygen and the Critical Point of Oxygen and Nitrogen. H. Kamerlingh Onnes, C. Dorsman and G. Holst (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 950—953. Compare A., 1913, ii, 1020).—The vapour pressure

of pure liquid oxygen was determined between −155° and the critical temperature. The vapour pressure increases from 9·096 atm. at −154·91° to 49·640 atm. at −118·70°. The critical data are given as $\theta_k = -118·84°$ and $p_k = 49·713$ atm. The value of RT_k/p_kv_k, where the critical volume v_k is derived from the law of the rectilinear diameter, is equal to 3·419 instead of 3·346, as recorded previously.

In connexion with the determination of the critical temperature, the authors call attention to the fact that no critical opalescence was observed, although this phenomenon was specially looked for.

H. M. D.

Isothermals of Diatomic Substances and their Binary Mixtures. XVI. Vapour Pressures of Nitrogen between the Critical Point and the Boiling Point. C. A. Crommelin (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 959—962. Compare preceding abstract).—The vapour pressure of pure liquid nitrogen has been measured at temperatures between −191·88° ($p = 1·4727$ atm.) and −148·85° (30·364 atm.). The observations agree fairly well with the pressures calculated from the formula $\log p = 5·76381 - 853·522/T + 54372·3/T^2 - 1783500/T^3$. The constants in this equation correspond with the critical data $p_k = 33·49$ atm. and $\theta_k = -147·13°$.

H. M. D.

The Rectilinear Diameter of Nitrogen. E. Mathias, H. Kamerlingh Onnes and C. A. Crommelin (*Compt. rend.*, 1915, **160**, 237—239; *Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 953—959. Compare A., 1911, ii, 203; 1912, ii, 900).—The authors have determined the density of liquid nitrogen and of the saturated vapour over the range of temperature between the solidification point and the critical point, and have compared the values with the results already obtained for argon and oxygen (*loc. cit.*). Leaving out the values for the three degrees below the critical temperature, the values for the diameter of nitrogen deviate but very slightly from a straight line, which, however, shows a convex curvature towards the temperature axis at the low temperatures. By extrapolation the critical density of nitrogen at its critical temperature, −147·13°, is found to be 0·31096, from which the critical coefficient is calculated to be 3·421, a value very close to those obtained for argon and oxygen.

W. G.

History of Continuous Cooling in Distillation. Edmund O. von Lippmann (*Chem. Zeit.*, 1915, **39**, 1—3).—A critical examination of the literature bearing on the development of the process of distillation in the fifteenth and sixteenth centuries.

G. F. M.

Vapour Pressure of Acetone-Chloroform Mixtures in Relationship to the Temperature. The Association of Acetone. E. Beckmann and O. Faust (*Zeitsch. physikal. Chem.*, 1914, **89**, 235—246).—Making use of the pressure regulator previously described (A., 1914, ii, 621), the vapour-pressure curves of mixtures

of acetone and chloroform have been determined at 55·10°, 40·40°, and 28·15°. The method consists in an analysis of the distillate and residual mixture in the boiling flask. The analysis is carried out refractometrically, using a Pulfrich refractometer. The vapour pressures obtained in the various cases are compared with those calculated according to the Dolezalek theory (A., 1909, ii, 22; 1910, ii, 184), from which it is shown that acetone is associated and to an increasing extent as the temperature is lowered. The mass-action constant for the formation of the chloroform–acetone complex is worked out and found to be at 55·10° 1·03, at 40·40° 1·33, and at 28·15° 1·53. J. F. S.

Ebullioscopic Behaviour of Solvents at Different Pressures. III. Aniline, Phenol, Naphthalene and Diphenyl. E. BECKMANN and O. LIESCHE [with J. VON BOSSE, K. HARING and W. WEBER] (*Zeitsch. physikal Chem.*, 1914, **89**, 111—124. Compare A., 1912, ii, 621, 622).—The ebullioscopic constants of aniline and phenol have been determined at thirteen different pressures from 760 mm. to 150 mm., naphthalene at four pressures from 763 mm. to 172 mm., and diphenyl at the three pressures, 754, 458, and 188 mm. It is shown that aniline and phenol are very similar in their ebullioscopic behaviour. The constants are very close together even at reduced pressures. The experimental values of the constants agree well with the calculated constants, except those obtained from the Walden formula, and in this case the divergence is greater in the case of phenol than in that of aniline. This points to a greater association in the case of phenol, and also that aniline is not a strictly normal liquid, even though the association is only slight. The constants obtained experimentally for naphthalene and diphenyl agree satisfactorily with the theory. It is therefore shown that the calculation of the ebullioscopic constants from critical data is allowable in the case of high boiling liquids. The newly-determined values of K are: aniline, 36·9; phenol, 36·0; naphthalene, 58·0; and diphenyl, 70·6. J. F. S.

Allotropy of Cadmium. V. ERNST COHEN and W. D. HELDERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1050—1054. Compare this vol., ii, 40).—The absorption of heat which accompanies the transformation of α-cadmium into γ-cadmium has been obtained directly by measurement of the *E.M.F.* and the temperature-coefficient of cells arranged according to the scheme Cd | cadmium sulphate solution | 8% cadmium amalgam, one cell containing α-cadmium as electrode and the other γ-cadmium. The *E.M.F.* of the α-cadmium cell is given by $E_\alpha = 0{\cdot}04742 - 0{\cdot}000200(t - 25°)$, and that of the γ-cadmium cell by $E_\gamma = 0{\cdot}05047 - 0{\cdot}0002437$ $(t - 25°)$. By means of the Gibbs-Helmholtz equation, the above measurements yield 739 cal. for the difference between the heats of dissolution of 1 gram atom of γ- and α-cadmium in an unlimited quantity of 8% amalgam at 18°. This, therefore, represents the quantity of heat which is absorbed in the transformation of α-cadmium into γ-cadmium at 18°.

The temperature, at which $E_\alpha = E_\gamma$, represents the transition temperature corresponding with this allotropic change, and from the above equations this temperature is found to be 94·8°.

H. M. D.

Unstable Chromium Sesquioxide and Corrections of Previous Work on the Heat Effect of Chromium and Aluminium Sesquioxides in Fusions with Sodium Peroxide. W. G. MIXTER (*Amer. J. Sci.*, 1915, [iv], **39**, 295—299).—Owing to an error in calculation the heat effect for one mol. of chromium sesquioxide reacting with sodium peroxide was wrongly given in a previous paper (A., 1908, ii, 929); it should be 109·4 Cal. The sesquioxide used in the determinations was made by heating the hydroxide over a blast lamp; essentially the same value was found for the crystalline oxide, which would seem to indicate that the ignited oxide was crystalline. Microscopic examination, however, showed no appearance of crystals.

Amorphous chromium sesquioxide glows when heated at temperatures between 500° and 610° (compare Endell and Rieke, A., 1914, ii. 471). Experiments on hydroxides which had been heated at temperatures from 320° to 420° in hydrogen, and which still contained water and carbon dioxide, gave 865 cal. for the heat of reaction of 1 gram of unstable chromium sesquioxide with sodium peroxide. If the heating is sufficiently prolonged at 400° the stable oxide is produced, the heat effect then being 687 cal., which is slightly lower than the value, 720 cal., for the ignited sesquioxide.

The author now gives the following corrected results: $2Cr + 3O = Cr_2O_3$(cryst.) + 267 Cal.; $2Cr + 3O = Cr_2O_3$ (stable, amorph.?) + 266 Cal.; $2Cr + 3O = Cr_2O_3$(unstable) + 243 Cal. approx.

New determinations of the heat of reaction of amorphous alumina, made by heating the hydroxide for fifteen minutes over the blow-pipe, with sodium peroxide, allowing for the heat effect of the oxygen set free, gave $Na_2O + Al_2O_3 = 2NaAlO_2 + 55·1$ Cal. Corundum gave the value 48·0 Cal.; and aluminium hydroxide, which had been heated at 500° for twenty-four hours, gave 59·4 Cal., not making any correction for the 1·7% of water it contained. The latter value indicates that alumina which has been nearly dehydrated at 500° polymerises at higher temperatures. T. S. P.

Thermochemical Investigations. W. A. ROTH and K. VON AUWERS (*Annalen*, 1915, **407**, 109—111).—The thermochemical investigations, commenced in 1910 and discontinued until the unusual difficulties, partly technical and partly chemical, associated with the method had been overcome (compare following abstract), are now being resumed. C. S.

Manipulation of the Calorimetric Bomb. Calculation of Heats of Combustion. W. A. ROTH (*Annalen*, 1915, **407**, 112—133. Compare A., 1910, ii, 584).—The following subjects are discussed: (1) The correction for the exchange of heat with the

surroundings. (2) The determination of the water-equivalent of the apparatus. It is shown that the mere exchange of one thermometer for another affects the value. (3) The use of benzoic acid and of sucrose for calibration purposes. (4) The calibration of the apparatus by an electrical method. The difference between this and the thermal method is only about 0·1%. (5) Factors to be used in comparing the thermochemical data of different investigators. (6) In many cases the molecular heat of combustion of a liquid or solid substance can be roughly calculated by multiplying by 52·2 the number of atoms of oxygen required for the complete combustion of one molecule of the substance. C. S.

Combustion of Volatile Substances in the Calorimetric Bomb. W. A. ROTH and H. WALLASCH (*Annalen*, 1915, **407**, 134—145).—It is well known that the combustion of the vapour of a volatile substance is incomplete even in the presence of a large excess of oxygen. The authors have tested the methods of overcoming this difficulty proposed by various investigators, and come to the conclusion that no method is applicable universally. In the "protective" methods the use of combustible envelopes is not recommended; glass envelopes are preferable. The following devices, arranged in order of increasing efficiency, are recommended: glass vessels with small caps of gelatin, or, better, celluloid; enclosure of the platinum combustion dish by a glass cover sealed with vaselin, or, best of all, by a "cellon" or "cellophan" cover sealed with vaselin. C. S.

Heats of Combustion of Aromatic Hydrocarbons and of their Hydrogenised Derivatives. W. A. ROTH and K. VON AUWERS (*Annalen*, 1915, **407**, 145—176).—Careful and accurate as are Stohmann's researches on the subject (1890—1893), the fact cannot be disregarded that his method of treating volatile substances is not above suspicion (compare preceding abstract); moreover, many of his compounds, particularly *cyclo*hexane and *cyclo*hexadiene, cannot, in the light of present-day knowledge, have been individual. The influence of the conjugated system of double linkings on the heat of combustion was first recognised by Thiele in 1899. Consequently Stohmann's thermochemical law of the hydrogenation of aromatic substances cannot be accepted without further investigation. The authors indeed find that the law is certainly not true; in the series they have examined, the difference between the heats of combustion of the di- and the tetra-hydro-derivatives is not the same as that between those of the tetra- and the hexa-hydro-derivatives. They have confined their experiments to hydrocarbons, of the purity of which there can be no question, and have determined their heats of combustion with all the modern refinements (preceding abstracts). The following values (Cal.) of the molecular heat of combustion at constant pressure and at the specified temperature have been determined: benzene, 782·3/20·4°; *cyclo*hexene, 893·7/21·0°; *cyclo*hexane, 938·5/17·4°; toluene, 935·2/19·0°; 1-methyl*cyclo*hexene, 1049·6/15·7°; *m*-xylene, 1089·5/20·6°; 1:4-di-

methyl-$\Delta^{1:3}$-*cyclo*hexadiene, 1153·7/19·5°; 1-ethyl*cyclo*hexene, 1205·4/14·9°; 1-methyl-4-ethyl-$\Delta^{1:3}$-*cyclo*hexadiene, 1312·5/20·0°; 1-methyl-4-*iso*propyl-$\Delta^{1:3}$-*cyclo*hexadiene, 1472·2/20·5°; naphthalene (solid) 1235·2, (liquid) 1239·7; Δ^{1}-dihydronaphthalene, 1297·8/20·5°; Δ^{2}-dihydronaphthalene (solid) 1299·8/20·7°, (liquid) 1302·7; 1:2:3:4-tetrahydronaphthalene, 1341·2/20·0°; decahydronaphthalene, 1503·9/19·2°. These values are discussed in connexion with those obtained by Stohmann and by Zubov (A., 1913, ii, 385), and the following conclusions are drawn: (1) the presence of one methyl group scarcely affects the increase of the heat of combustion; (2) the increase produced by the addition of two hydrogen atoms to the aromatic hydrocarbon is certainly much greater than that due to the addition of hydrogen to the dihydro- and to the tetrahydro-compounds. The latter two increases are not the same. The difference between the heats of combustion of a conjugated *cyclo*hexadiene and the corresponding aromatic hydrocarbon is about 64 Cal. The difference is about 50 Cal., for a conjugated *cyclo*hexadiene and the *cyclo*hexene, and about 45 Cal. for the *cyclo*hexene and the *cyclo*hexane. (3) The heat of combustion of a substance containing a conjugated system of double linkings is smaller by a few Cal. than that of an isomeride which does not contain this structure. (4) In non-conjugated aliphatic compounds the difference between the heats of combustion of the hydrogenised and the non-hydrogenised substances is about 37 Cal. (5) Hydrogenation appears to be always an exothermic reaction. (6) In the case of naphthalene, as in that of benzene, the introduction of the first two hydrogen atoms has the greatest effect on the heat of combustion. C. S.

The Viscosity of the Vapour of Iodine. A. O. Rankine (*Proc. Roy. Soc.*, 1915, [*A*], **91**, 201—208).—The viscosity of iodine vapour has been determined by measurement of the rate of transpiration through a capillary tube. This tube was immersed in an oil-bath, the temperature of which was kept constant during the experiment, and iodine was allowed to distil through the capillary tube from a flask containing solid iodine at 100° and condensed in a well-cooled tube, which was connected with a reservoir containing air at a pressure of about 2 cm. of mercury. The observed rates of transpiration were corrected for the change in the dimensions of the capillary tube with change in temperature, and also for the slipping of the gas over the walls of the tube. The following are the values obtained for the viscosity $\times 10^4$ at different temperatures: 124·0°, 1·843; 170·0°, 2·038; 205·4°, 2·198; 247·1°, 2·397.

The value calculated for the constant C in Sutherland's equation $\eta = K \cdot T^{\frac{1}{2}}/(1+C/T)$ is $C=590$. The ratio T_c/C, where T_c is the critical temperature, is equal to 1·32. This compares with 1·28 for the ratio given by chlorine and 1·25 by bromine.

By extrapolation of Sutherland's equation, the viscosity of iodine vapour at the critical temperature is $\eta_c = 3{\cdot}58 \times 10^{-4}$, and the value of η_c^2/A, where A is the atomic weight, is equal to $1{\cdot}01 \times 10^{-9}$.

This compares with 1·02 and $1·03 \times 10^{-9}$ for chlorine and bromine respectively.

The empirical relations thus found to hold for the halogens have been previously shown to be satisfied by the data for the inert gases (compare A., 1911, ii, 87). H. M. D.

Surface Tension and Hydration in Solution. M. Padoa and G. Tabellini (*Gazzetta*, 1915, **45**, i, 99—106).—Surface tension measurements of a number of solutions have been made at different temperatures by the falling-drop method (compare Morgan and Stevenson, A., 1908, ii, 356; Morgan and Higgins, A., 1908, ii, 668), the values of k being calculated by means of the formula: $k=\lfloor p(M/d)^{\frac{2}{3}}-p_1(Md_1)^{\frac{2}{3}}\rfloor/(t_1-t)$, where p and p_1 are the weights of the drop, and d and d_1 the densities of the solution, at temperatures t and t_1, and M the mean molecular weight of the liquid. With N- and $3N$-solutions of ammonium chloride and N-solutions of cobalt chloride, sodium bromide, and magnesium chloride, the values obtained for k indicate a slight association between solvent and solute. With N-, $2N$-, and $3N$-solutions of hydrochloric acid the values of k at 30—40° and 40—50° are respectively 1·20—1·17, 0·73—0·93, and 0·73—0·72. Such low values indicate very marked association, and the diminution, at first rapid and then slow, as the concentration increases, seems to point to the fact that in the $3N$-solution the association has almost reached its maximum value. T. H. P.

Structure of the Capillary Layer, and the Avogadro Number. G. Bakker (*Zeitsch. physikal. Chem.*, 1914, **89**, 1—48).—A theoretical paper in which a theory of capillarity is developed and tested from the known data of a large number of liquids. It is shown that Gauss had erroneously regarded the surface tension as the intensity factor of the potential surface energy. The author shows that the surface tension can be regarded as the amount of the total divergence from Pascal's law. If p_N represents the vapour pressure and p_r the mean hydrostatic pressure in the direction parallel with the surface of the capillary layer, H the surface tension, and ζ the thickness of the capillary layer, then

$$H=(p_N-p_r)\zeta.$$

The value $p_r\zeta$ is the work done by the hydrostatic pressure p_r in the formation of the capillary layer per unit of surface, since ζ is the volume of the capillary layer per unit surface. The increase of the free energy is $-p_r\zeta$. whilst $p_r\zeta$ is the diminution of the free energy. The actual increase of the free energy is given, therefore, by $(p_N-p_r)\zeta$, and the so-called capillary energy by $H=(p_N-p_r)\zeta$, which has the same numerical value as the surface tension. The theories of Gauss and Laplace are in the same respect shown to be incomplete, since it is impossible to build up a complete theory of liquids and capillarity by means of attractive forces alone, without making use of an antagonistic or opposing force. In the present theory the idea of substance, as in the Laplace theory, is replaced by a constant medium (Agens), and as the

potential function of the attractive forces between its elements the function $-fe^{-r/\lambda}/r$ is accepted. This is done on four different grounds: (1) The density gradient of the medium substituted for the substance is always finite (van der Waals). (2) It is the only function which represents the attraction of a homogeneous sphere on an outside mass as a continuously decreasing function of the distance between the centre of the sphere and the outside mass. (3) The cohesion of the medium can be expressed as a surface integral in the same way as the medium in the Maxwell theory of electricity and magnetism, and (4) the coefficients of the cohesion expressions for the homogeneous media of Laplace, Gauss, and Poisson contain the same value. The thickness, ζ, of the capillary layer is expressed by the formula $\zeta=\gamma.H/a(\rho_1-\rho_2)^2$, where H represents the surface tension, a the Laplace constant in the cohesion formula, and ρ_1 and ρ_2 the densities of the liquid and vapour respectively, and γ is a constant which has a value between 15 and 17. If N represents the Avogadro number, that is, the number of molecules in a gram-molecule of a substance, Mr_i the internal molecular heat of vaporisation, $[M\epsilon_s]$ the molecular capillary energy (not the free energy), and i a factor having a numerical value approximately 0·39, then at low temperatures and for non-associated substances $\sqrt[3]{N}=iMr_i/[M\epsilon]_s$. If the N value $6\cdot2\times10^{23}$, as found by Rutherford, Geiger, and Planck, is adopted, the above formula gives $i=0\cdot38$, whereas the value $N=6\cdot85\times10^{23}$ as found by Perrin gives $i=0\cdot39$, consequently the present theory is more nearly in accord with the Perrin value. In the case of associated substances the value of i is much smaller than in the case of non-associated substances, which is also in keeping with the theory. The analytical meaning of i at low temperatures is given by the formula $i=n_1(1+q)$, where n_1 is the number of molecular layers in the capillary layer, and q is given by the expression

$$q=(\epsilon_2-\epsilon)/(\epsilon-\epsilon_1),$$

where ϵ_1 is the energy of the liquid, ϵ_2 the energy of the vapour, and ϵ that of the capillary layer, per unit mass. If the change from liquid to vapour takes place in a discontinuous manner, then $n_1=1$ and $q=1$, so that $i=0\cdot5$ instead of 0·39—0·40, as is given by the experimental data and demanded by the theory for simple substances. For complicated compounds the value is a little below 0·39; for example, ethyl ether at 15·5° has a value $i=0\cdot387$, and benzene at 20° has a value $i=0\cdot378$. The present theory does not, therefore, take into consideration the cases where a discontinuous change from liquid to vapour occur, and consequently does not apply to them. J. F. S.

Ion Diffusion in Permutite and Natrolite. GÜNTHER SCHULZE (*Zeitsch. physikal. Chem.*, 1914, **89**, 168—178).—Permutite, a hydrated sodium aluminium silicate used largely for softening water, and natrolite, a natural zeolite, both possess the property of exchanging their sodium atoms for other metallic atoms when immersed in solutions of salts. Thus when immersed in silver nitrate solution as much as 93% of the sodium is replaced by silver.

A number of experiments on the replaceability of sodium by silver have been carried out, and as a result the rate of diffusion of the sodium has been calculated. The electrical conductivity has also been determined. From the fact that sodium and silver are interchangeable in permutite it is deduced that both silver and sodium are capable of diffusion in solid permutite. The exchange of sodium and silver is dependent on the ionic concentration of the silver, and not on the total concentration of the silver salt. Sodium permutite has an electrical conductivity at 20° of $6{\cdot}53 \times 10^{-4}$ ohms^{-1}, cms.$^{-1}$, whilst silver permutite has a value $4{\cdot}48 \times 10^{-4}$ ohm^{-1}, cms.$^{-1}$. From these values the diffusion constant is calculated, and shown to have the values $1{\cdot}30 \times 10^{-8}$ sq. cms. per sec., and $1{\cdot}90 \times 10^{-8}$ sq. cms. per sec. respectively. The volume of the pores in permutite is 30% of that of the total volume. The same diffusion constant is obtained from the diffusion experiments as from the conductivity experiments, when it is assumed that the active surface of the permutite is nine or ten times as great as that of an equally large non-porous mass. The diffusion constant of natrolite is $1{\cdot}48 \times 10^{-10}$ sq. cms. per sec. J. F. S.

Soret's Phenomenon. Th. Wereide (*Ann. Physique*, 1914, [ix], **2**, 55—66).—If two parts of a solution are maintained at different temperatures, diffusion takes place, and the resulting distribution of the dissolved substance should theoretically depend on the ratio of the absolute temperatures of the two parts of the solution. Further experiments to determine the influence of the temperature on the distribution have been made with a modified form of apparatus, in which the total height of the column of solution is reduced to 15 mm. In this way, the time necessary for the attainment of equilibrium has been diminished to a very large extent as compared with the time required in Arrhenius' experiments, in which the length of the diffusing column of liquid was 15 cm.

Preliminary experiments with aqueous solutions of antipyrine showed that the velocity of diffusion diminishes with falling concentration of the original solution, that the ratio of the resulting concentration is greater than the theoretical ratio, and that the observed ratio decreases with falling concentration. By extrapolation a limiting value of the ratio corresponding with zero concentration may be obtained.

From the results obtained with other substances it appears that some, such as copper sulphate and sodium hydroxide, behave like antipyrine. For others, the observed ratio is less than the theoretical, and increases with falling concentration. This has been found with sodium chloride, sucrose, and glycerol. The limiting ratio in some cases approximates to the theoretical value, but this is not usually met with.

The results obtained with ethyl alcohol, acetone, boric acid, and aniline lead to the conclusion that a difference of temperature has no influence on the distribution of these substances in aqueous solution. H. M. D.

Diffusion of a Solution of Variable Concentration and Temperature. Th. Wereide (*Ann. Physique*, 1914, [ix], **2**, 67—83. Compare preceding abstract).—If c and c' denote the concentrations of the dissolved substance in two portions of solution which are maintained at the absolute temperatures T and T' respectively, then if the diffusion process is determined by osmotic forces, theory requires that the distribution of the dissolved substance should satisfy the relation $c/c' = T'/T$. The experimental results recorded in the previous paper show that this is by no means generally the case.

If, on the other hand, it is assumed that the movements of the molecules are of the Brownian type, that is to say, irregular and non-orientated, it can be shown that the distribution of the dissolved substance should be expressed by the equation:

$$c/c' = \sqrt{u'T'/uT},$$

in which u and u' represent the mobilities of the molecules at temperatures T and T'. It is also shown that c/c' will tend towards unity when the mobility of the molecules of the dissolved substance approaches that of the molecules of the solvent. In this way it is possible to account for the fact that certain substances show no evidence of diffusion under the influence of a temperature gradient. On the further assumption that many dissolved substances are hydrated in aqueous solution, and that both kinds of diffusion occur simultaneously, it is possible to give an explanation of the widely divergent behaviour exhibited by the substances investigated in the previous paper. H. M. D.

The Diffusion of Solutions. J. Thovert (*Ann. Phys.*, 1914, [ix], **2**, 369—427. Compare A., 1903, ii, 13; 1910, ii, 191).—Using his optical method already described (compare A., 1902, ii, 197, 384, 445, 599), the author has continued his studies on the diffusion of solutions, and has extended the work to solutions in which solvents other than water were used. The results obtained for the diffusion of an aqueous solution of sodium chloride in water confirm the direction of the variation of the coefficient of diffusion, D, with the concentration of the sodium chloride, as previously recorded (*loc. cit.*). The results obtained in a study of the diffusion of hydrochloric acid show a diminution in the coefficient of diffusion with the concentration, and they are not in agreement with those given by Öholm (A., 1905, ii, 147), who, using Graham's method, obtained numbers varying in the opposite sense and in agreement with Arrhenius' hypothesis. A further study of the diffusion of a solution of one electrolyte into that of another, or of an electrolyte into a non-electrolyte, shows that the displacement of the concentration of the solute upwards or downwards in the solution into which diffusion is taking place, must be due to some action quite distinct from the electrolytic effects dependent on electrolytic dissociation.

An examination of the diffusion of phenol in water and in a number of different types of organic solvents, simple or mixed, shows that there is a relationship between the diffusion of phenol

in different solvents and the viscosity of these liquids, the variations of D and of the inverse of the viscosity being parallel. This relationship is also borne out by examination of the diffusion of a very large number of organic compounds of different types in either water, methyl alcohol, or benzene as solvents. The results of this work are tabulated. The value of D for a given substance in methyl alcohol is almost double the value in water, and generally almost equal to the value in benzene. For the groups alcohols, phenols, nitrogenous compounds (other than nitro-compounds), and most of the acids, there is but slight variation in the value of the quotient, $D\sqrt{M}$ in each solvent, where M is the molecular weight of the substance dissolved. Of the substances soluble in water only three show any noticeable variation from this rule, namely, oxalic acid, picric acid, and aniline hydrochloride. The other types of substances are distinguished by varying values of $D\sqrt{M}$, the variations bearing no apparent relationship to the chemical constitution of the compounds, the halogen derivatives of hydrocarbons giving the highest values. W. G.

Influence of Colloidal Sulphur on the Freezing Points of Aqueous Solutions of Certain Electrolytes. M. Raffo and G. Rossi (*Gazzetta*, 1915, **45**. i, 119—122).—The authors have investigated cryoscopically the influence of colloidal sulphur on the freezing point of a solution containing its "crystalloids of formation," sodium sulphate and sulphuric acid (compare A., 1914, ii, 35; also Paternò and Cingolani, A., 1914, ii, 182), diluted with an equal volume of either water or a dilute solution of lithium chloride or sulphate, sodium sulphate, or sulphuric acid. The elevation produced in the freezing point by the presence of the colloidal sulphur is the same in all cases. The colloidal sulphur is, therefore, without influence on the freezing points of solutions of added electrolytes, even of sodium sulphate and sulphuric acid, although when these are present in the colloidal solution as "crystalloids of formation," the sulphur has a distinct effect on the freezing point. These results are in accord with those of conductivity measurements (*loc. cit.*), and show that, in presence of colloidal sulphur, the crystalloids of formation, sulphuric acid, and sodium sulphate are not able to conduct electricity or to lower the freezing point of water. T. H. P.

Determination of the Diffusion, the Velocity of Precipitation, and the Sedimentation Equilibrium of the Particles of Selenium and Gold Sols. Arne Westgren (*Zeitsch. physikal. Chem.*, 1914, **89**, 63—90).—The partition of the particles of several gold sols and a selenium sol, which had been allowed to sediment until equilibrium was established, was measured by a method similar to that used by Perrin. By centrifuging the particles were oriented on a straight line boundary of a microscopic chamber, and then the partition brought about, by diffusion, was determined after a time τ. The formula $\tau \cdot \log(v_1/v_2)/(x_2^2 - x_1^2) = Nf/4RT$ was deduced to represent the partition, where v_1 and v_2 represent the concentra-

tion of the particles at distances x_1 and x_2 from the straight-line boundary, N is the Avogadro constant, f the viscosity, R the gas constant, and T the absolute temperature. The velocity of precipitation was determined by two methods, partly by the determination of the number of particles which settled in a given time in a parallel walled vessel, from which a height-concentration diagram was made, and partly by direct observation of a quantity of particles which had been pressed to the bottom of the vessel by centrifuging. As a result of the experiments it is shown that the Einstein formula is absolutely true for the Brownian movement of the particles of the sols investigated. The mean kinetic energy of a particle appears to be independent of its mass, and Stokes' law is accurate within the experimental error, which is approximated as about 5%. The Avogadro constant is determined as $(60{\cdot}6 \pm 2) \times 10^{22}$, which is not very different from $(60{\cdot}6 \pm 0{\cdot}1) \times 10^{22}$ as found by Millikan. J. F. S.

Colloidal Mercuri-organic Compounds. III. M. Raffo and G. Rossi (*Gazzetta*, 1915, **45**, i, 132—139. Compare this vol., ii, 152).—Experiment shows that there exists between the colloids, tetra- and penta-mercuriacetanilide acetates, and the acetic acid which is formed with them, a peculiar electrical equilibrium completely analogous to that existing in solutions of colloidal sulphur between the colloid and the crystalloids, sulphuric acid and sodium sulphate. In either case this equilibrium is manifested as a diminution in the electrical conductivity of the crystalloids of formation. Addition of a crystalloid capable of coagulating the colloid is accompanied by a decrease of the conductivity, owing to the transference of electric charges from the coagulating crystalloid, and from the crystalloids of formation to the colloidal particles.

T. H. P.

Colloidal Solutions in Chloroform. H. Freundlich and John A. Gann (*Intern. Zeitsch. phys.-chem. Biol.*, 1915, **2**, 1—18).—Solutions of pure fats or spermaceti in chloroform when shaken with methylene-blue or other basic dyes do not become more deeply coloured than chloroform itself after similar treatment. These substances, therefore, are not present in colloidal form in the chloroform, and this conclusion is confirmed by measurements of the molecular weights by Barger's microscopic method.

On shaking a slightly acid solution of spermaceti or fat in chloroform with an aqueous sodium hydroxide solution, an emulsion is obtained, of which the disperse phase consists of ultramicroscopic particles composed probably of minute drops of soap solution with protective coverings of soap-containing material. This fat-chloroform emulsion can be washed with water, and if methylene-blue is then introduced, it is adsorbed by the emulsion until a definite equilibrium point is reached. The combination of methylene-blue with a chloroform solution of slightly acid tristearin is also an adsorption process.

The results obtained by the author lead to the conclusion that

the disperse phases of the colloidal solutions of lipoids in chloroform described by Loewe (A., 1912, ii, 742) also probably consist of aqueous solutions. H. W. B.

The Behaviour of Colloids toward Pure and Mixed Liquids. I. The Systems Caoutchouc–Benzene–Alcohol and Caoutchouc–Benzene–Acetone. William Augustus Caspari (*Trans.*, 1915, **107**, 162—171).—The equilibrium diagrams for the above-mentioned systems have been experimentally determined. In order to obtain the whole diagram three methods were employed: (1) A benzene solution of de-resinified caoutchouc was titrated with alcohol until separation into two phases set in. Each limiting triad thus obtained gives a point on the binodal curve. The method, however, serves only over a short range on account of the high viscosity of the benzene solutions of caoutchouc. Then knowing the quantities of caoutchouc, benzene, and alcohol, the "synthetic volumes" could be calculated. (2) Proceeding in the same way, but adding an excess of alcohol, two fluid layers were formed in equilibrium, the lower of which contained the bulk of the caoutchouc. The composition of the two layers gave further points on the binodal curve. The upper layer was analysed, caoutchouc being obtained by evaporation, and the ratio of benzene to alcohol by refractive index measurements. From the relative volumes of the two layers and a knowledge of the composition of the upper layer, the composition of the lower layer was deduced. This method also breaks down when the precipitated clot contains too much caoutchouc to assemble into a homogeneous layer, and the binodal curve could only be continued by method 3. Precipitation was effected as before, the liquid phase which is now free from caoutchouc was analysed refractometrically, the clot was removed, dried between filter-papers, and transferred to a volumenometer charged with a benzene–alcohol mixture, and its volume determined. Similar determinations were made by the first and third methods when acetone was substituted for alcohol. All the measurements were made at 20°, and from the results isothermal diagrams are constructed on trilinear co-ordinates. With an increase in temperature the caoutchouc becomes less easily precipitable by alcohol and acetone. The presence of moisture in the precipitating liquid has the opposite effect to an increase in temperature, that is, the caoutchouc is more easily precipitated. From the results it is shown that at 20° caoutchouc is practically insoluble in a mixture of forty-three volumes or more of absolute alcohol and one hundred of benzene, and also in a mixture of eighty volumes or more of acetone and one hundred of benzene. A discussion of the form of the binodal curves completes the paper. J. F. S.

Velocity of Formation and Solution, and the Swelling, of Jellies. I. Traube and F. Köhler (*Intern. Zeitsch. phys.-chem. Biol.*, 1915, **2**, 42—84).—The authors have investigated the effects of the addition of various substances on the rate at which gelatin solutions gelatinise, and also on the rate of re-solution of the gel, the

methods being similar to those employed by Schryver (A., 1914, i, 616) in the case of cholate gels. The formation of the gel is hindered by chloroform, ether, and other narcotics, a large number of which were tested. The solution of the gel, on the other hand, is accelerated, and when the narcotics are arranged in the order corresponding with the degree to which they hinder the formation of the gelatin gel, it is found to be practically the same order as that for the acceleration of gel solution. Non-electrolytes, such as glycerol and the sugars, which increase surface tension, accelerate gel formation, and correspondingly inhibit gel solution.

Acids in amounts of less than 0·01 mol. per litre increase the rate of gel formation. Above this concentration they exert an inhibiting action, which reaches a maximum when the solution contains 0·019 mol. of almost any acid per litre. The rate of solution of the gel is affected in exactly the reverse manner. Bases similarly inhibit formation and accelerate solution of the gel. Salts, in the case of dilute gelatin solutions, accelerate formation and inhibit solution of the gel, the extent of influence being represented by the order Ca–K–Na for cations and trichloroacetate–salicylate–iodide–bromide, cyanide – nitrate – chloride – sulphate – citrate for anions, the foremost in each series exerting the strongest action. With larger concentrations of the gelatin, the order becomes changed.

Alkaloidal salts behave in a similar way, provided the gelatin solution is dilute. With more concentrated solutions the effect is reversed. Consequently for certain strengths of gelatin solution, pilocarpine, which has the greatest accelerating action on gel formation in dilute gelatin solutions, and atropine, which has the least, become antagonistic. Similar antagonism occurs between non-electrolytes which lower surface tension and those which raise it; between narcotics and peptone, narcotics and salts, and between various salts, particularly between a calcium and the corresponding sodium salt.

The authors show that a complete analogy exists between the swelling of colloids and the formation and re-solution of gels. The greater the effect of an agent on the velocity of gel solution or formation, the greater is the effect on the capacity of colloids for swelling. The concentration of acid which produces the maximum inhibiting action on gel formation is approximately that which has the greatest effect on imbibition.

The authors point out the bearing of these results on the problems of narcosis, hæmolysis, chemotaxis, inflammation, mechanism of muscle contraction, production of œdema, etc. H. W. B.

Gas Equilibria and a Test of J. D. van der Waals, jun.'s Formula. II. F. E. C. Scheffer (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1011—1026. Compare this vol., ii, 46).—A further discussion of gaseous equilibria on the lines indicated in the first paper (*loc. cit.*). The experimental data considered are those relating to the dissociation of iodine, hydrogen chloride, bromide, and iodide. The dissociation constants for the halogen hydrides lead

to values for the quotient of the moments of inertia which are in agreement with those calculated from the molecular radii.

H. M. D.

The Exchange of Atoms between Solid and Liquid Phases. G. VON HEVESY (*Physikal. Zeitsch.*, 1915, **16**, 52—55).—Experiments are described which have enabled the author to measure the rate of molecular exchange at the surface of separation of solids and liquids. The observations were made on lead and its compounds, and measurements of small changes in the distribution of lead at the contact surface were made possible by the addition of traces of thorium-*B*, which is an isotope of lead, to the liquid or solid phase.

In this way, observations have been made on the molecular exchange between solid lead chloride and a saturated solution of the salt, and at the surface of contact of metallic lead and lead dioxide and solutions of lead nitrate of varying concentration. The rate of exchange at the surface of metallic lead in contact with a solution of lead nitrate containing thorium-*B* is of such magnitude as to suggest that the exchange is not that which corresponds with complete thermodynamic equilibrium, but is due to the action of "local currents." At some points lead passes into solution, and at others separation takes place.

At the surface of contact of pure lead dioxide and a solution which contained lead nitrate (0·001*N*) and nitric acid (0·001*N*) and was saturated with "infected" lead dioxide, the rate of exchange was found to be very much smaller. In this case it is possible that the observed rate corresponds approximately with the kinetic exchange which would be found in a condition of thermodynamic equilibrium.

H. M. D.

Action of Ammonia Gas on the Hydrochlorides of Primary Amines. F. BIDET (*Ann. Chim.*, 1914, [ix], **2**, 132—188).—A résumé of work already published (compare A., 1912, ii, 915; 1913, ii, 197, 572).

W. G.

Calculation of the Equilibrium Constant from Cryoscopic Measurements. Calculation of the Degree of Hydrolysis. J. B. GOEBEL (*Zeitsch. physikal. Chem.*, 1914, **89**, 49—62).—A theoretical paper in which the author calculates the ionisation constant and degree of dissociation of a number of acids, alkali salts, and sucrose from cryoscopic measurements of these substances by other investigators. It is shown that the equation for the calculation of the number of molecules (C_r) from the freezing-point lowering (Δ) can with advantage be changed from its original form, $C_r = 0{\cdot}705 \log_{10}(1+\Delta) + 0{\cdot}24\Delta + 0{\cdot}004\Delta^2$, to

$$C_r = 0{\cdot}705 \log_{10}(1+\Delta) + 0{\cdot}24\Delta + 0{\cdot}004\Delta^2 - 0{\cdot}0002\Delta^6,$$

in certain cases. Both formulæ are practically identical for values of Δ up to 1·2°; only in the case of greater values of Δ, particularly those above 2°, does the second formula give somewhat smaller values for C_r, and in consequence it yields good values in the case of sucrose solutions for $\Delta = 0°$ up to $\Delta = 2{\cdot}7°$. On applying the modified equation to solutions of strong binary acids it is shown

that over a wide concentration interval a very good value for $k=C_2^2/C_1$ is obtained. This constant k is proportional to the decomposition values of Le Blanc, and if the relationship is expressed by z, then the expression $k=0{\cdot}33/z^3$ holds with good approximation. In connexion with binary salts the following rules were derived: (1) The ordinarily calculated dissociation constant shows that the solution contains either complex ions or complex molecules or both. (2) The double molecule concentration (A_2B_2) in binary salts of the type AB can be regarded as the mean of the complex-ion concentrations, $\frac{1}{2}(A_2B+AB_2)$, if it is assumed that few or no double molecules exist in the solution. The dissociation constant k of a number of alkali salts shows a fall in the value as the concentration rises, and from the nature of this fall, certain regularities are apparent. The degrees of hydrolysis of sodium acetate and sodium carbonate were calculated, and values obtained which agree exactly with the experimental results of Shields (A., 1893, ii, 448). In this calculation the dissociation constants calculated by the modified formula were made use of. J. F. S.

Apparent Slowness of the Hydrolysis of Ferric Salts. A. Quartaroli (*Gazzetta*, 1915, **45**, i, 139—152).—In order to throw light on the non-instantaneous character of the hydrolysis of ferric salts in aqueous solution, the author has investigated the change of the electrical conductivity and magnetic susceptibility with time, and the final concentration of the hydrogen ions in ferric chloride solutions diluted to various extents. From the results obtained the conclusion is drawn that, immediately after the dilution, the hydrolysed portion of the salt is composed partly of the ions $Fe\dot{O}H$ (and possibly $Fe\dot{O}_2H_2$) and partly of amicroscopic, colloidal granules of $(FeO_2H_3)_x$ or highly basic chlorides, these having a high degree of dispersion, and, in consequence of their enormous surface, absorbing a considerable quantity of hydrochloric acid. Contrary to Goodwin's hypothesis (A., 1897, ii, 16), the amount of colloidal ferric hydroxide remains unaltered from the beginning to the end of the reaction; the degree of dispersion alone diminishes, the decrease thus effected in the surface causing liberation of a part of the hydrochloric acid. As the dilution increases, the fraction of the hydrolysed part consisting of ordinary ionised molecules, FeOH, FeO_2H_2, etc., increases in comparison with that existing in the colloidal state.

Various authors have stated that, in a solution of 0·000054-molar concentration, ferric chloride is completely hydrolysed, and exists wholly in the colloidal condition, but by means of the author's sensitive method for determining the magnetic susceptibility (A., 1914, ii, 619) it is shown that this statement is erroneous. The failure of the reaction with potassium ferrocyanide at this dilution and its appearance when hydrochloric acid is added are indecisive in this matter, since it cannot be asserted that the reactions of the ion, $Fe^{\cdot\cdot\cdot}$, are the same as those of the ion, $(FeOH)^{\cdot\cdot}$ or $(FeO_2H_2)^{\cdot}$.

T. H. P.

Velocity of Solution of Metals in Acids. II. Velocity of Solution of some Zinc-Copper Alloys in Hydrochloric Acid. M. CENTNERSZWER and JS. SACHS (*Zeitsch. physikal. Chem.*, 1914, **89**, 213—229. Compare A., 1914, ii, 550).—The velocity of solution of zinc-copper alloys, containing 0·51—9·75% copper, in hydrochloric acid of various concentrations, has been determined at 25°. The alloy was cut into thin discs, and mounted at the end of a rotary stirrer, and all but the face covered with wax; this was then placed in hydrochloric acid, and rotated 100 times per minute. The hydrogen evolved was collected, and its volume measured, from which the velocity of solution was deduced. It is shown that no copper passed into solution. The alloys all exhibit an induction period, which is considerably shorter than that observed in the case of pure zinc. The velocity constant decreases rapidly immediately the induction period is at an end, and finally reaches a limiting value. The velocity of solution decreases with increasing copper content. "Activated" plates show a regular rate of solution, and obey Boguski's law. Slowly cooled alloys have a longer induction period, but a greater velocity of solution than rapidly cooled plates. J. F. S.

The Wet Oxidation of Metals. IV. The Question of Passivity. BERTRAM LAMBERT (*Trans.*, 1915, **107**, 218—222).—A theoretical paper in which the author compares the action of water on pure iron with its action on passive iron. The action in both cases is very similar, and all the usual tests for passivity of iron yield the same results with pure iron. From these results he draws the conclusion that the inactivity of pure iron is the result of its possessing a physically homogeneous surface, and by analogy iron which has been rendered passive must possess a physically homogeneous surface of some kind which is not necessarily always the same. Such a surface would cause the iron to have the same potential in all parts, and in consequence there would be no tendency for it to pass into solution. He therefore defines passivity as the production, by some chemical or electrochemical process, of a physically homogeneous layer on the surface of a metal which originally was physically heterogeneous. J. F. S.

Theory of Gas Reactions. HEINRICH LÖWY (*Ann. Physik*, 1915, [iv], **46**, 561—568).—A theoretical paper in which it is shown that Liebig's hypothesis, that the action of catalysts consists in the transmission of the molecular vibrations of the catalyst to the molecules of the reacting substances, may be submitted to experimental test by application of the quantum theory to suitable gas reactions. H. M. D.

The Use of Nickel and its Oxides in Catalysis. J. B. SENDERENS and JEAN ABOULENC (*Bull. Soc. Chim.*, 1915, [iv], **17**, 14—19. Compare A., 1912, ii, 770; Bedford and Erdmann, A., 1913, i, 707; Ipatieff, A., 1907, i, 5, 6, 827, 828).—A discussion as

to whether the catalytic action of finely divided nickel or its oxides is due to the metal itself or its oxide. Finely divided metallic nickel can be used as a catalyst for hydrogenations either by the wet or the dry method. The oxides of nickel are apparently inactive by the dry method, but by the wet method possess an activity which cannot be attributed to the presence of some reduced nickel. The relative activity of the oxides or the metal depends on the manner in which they have been prepared. W. G.

Catalytic Addition of Hydrogen to Unsaturated Compounds. Detection of Metallic Nickel in the Hardening of Oils, using Oxides and other Compounds of Nickel. W. Normann and W. Pungs (*Chem. Zeit.*, 1915, **39**, 29—31, 41—42).—The experiments of Meigen and Bartels (A., 1914, i, 482), which indicated that the oxides of nickel could not, without reduction to metallic nickel, act as hydrogenating catalysts as was maintained by Bedford and Erdmann (A., 1913, i, 701), have been repeated by the authors with some modifications in detail, and in every case, after the hardening of the oil, the presence of free metallic nickel in the catalyst which previously contained no free metal, has been conclusively demonstrated on the grounds of electrical conductivity, analytical determinations, and the formation of nickel carbonyl. Cotton-seed, olive, linseed, and sesame oils were used, and the reduction was carried out at 250° by passing a rapid stream of hydrogen through the oil in presence of 1% of nickel oxide. After two to three hours the catalyst was separated, washed with benzene, and fragments separated by means of a magnet were found to be good electrical conductors. Analyses of that portion of the recovered catalyst which was soluble in sulphuric acid showed, from the volume of hydrogen evolved, free nickel contents varying from 71·4 to 86·5%, much higher than could be accounted for by any assumption of a suboxide. For the preparation of the nickel carbonyl, the catalyst was not removed from the fat, but after cooling to from 50° to 90° the stream of hydrogen was replaced by carbon monoxide, and the evolved gases passed through a hot tube. In every case nickel mirrors were obtained corresponding with at least from 4% to 7% of the weight of the catalyst originally taken, which quantity spread over the surface of the inactive oxide would, it is declared, be sufficient to account for the reducing activity observed. It is concluded, therefore, that a reduction with molecular hydrogen in the absence of free metal has not yet been carried out, and that the assertion that anything other than the free metal acts as a catalyst is absolutely unproved.

This conclusion is in direct contradiction to that recently arrived at by Senderens (preceding abstract). G. F. M.

Catalysis in the Oxidation of Alkali Sulphites. Émile Saillard (*Compt. rend.*, 1915, **160**, 318—320).—An enquiry into the effect of certain substances, likely to be present in sugar juices, and syrups, on the rate of oxidation of the alkali sulphites formed

during the process of manufacture. The oxidation of alkali sulphites is retarded by the presence of sucrose, invert sugar, the non-saccharine material as a whole, ammonium oxalate, glycerol, alkali hydroxides or carbonates, asparagine, glutamic acid, and potassium lactate. Between the experimental limits of temperature (15—90°) rise in temperature accelerates the oxidation, whilst increase in sugar content lowers the rate of oxidation. In molasses the oxidation of alkali sulphites is very difficult owing to the high sugar content (50%). Substances which accelerate the oxidation of alkali sulphites are nickel, zinc, aluminium, oxide of iron, manganese dioxide, calcium carbonate, marble, fire-brick, calcium sulphite, calcium phosphate, magnesium carbonate, calcium oxalate, alumina, and calcium sulphate, all in the form of powder. W. G.

Studies in Catalysis. Part II. The Inversion of Sucrose. ALFRED LAMBLE and WILLIAM CUDMORE MCCULLAGH LEWIS (*Trans. Chem. Soc.*, 1915, **107**, 233—248).—A series of measurements have been made of the rate of inversion of sucrose at 25°, 35°, and 45° by hydrochloric acid, of various strengths from $2{\cdot}429N$ to $0{\cdot}0502N$. The temperature-coefficients of the reaction have been calculated from the experimental results, and their change with the concentration of the hydrochloric acid has also been established. Assuming that both the undissociated hydrochloric acid as well as the ions catalyse the reaction, there is a slight fall in the critical increment (E) as the concentration of the catalyst increases; the critical increment being defined as the extra amount of energy required by 1 gram-molecule of the system according to the Rice-Marcelin equation, $d\log k/dT = E/RT^2$. Generally it has been found that for reversible reactions the larger the velocity constant the smaller the value of E, and vice versa. This also holds when the nature of the solvent is altered by the addition of a second solvent. The above-mentioned conclusions are in agreement with the Rice modification of the Marcelin equation, and also with the view that chemical reactivity is due to infra-red radiation emitted by the catalyst and absorbed by the reacting or decomposing substances. The possible catalytic action of the undissociated molecule is discussed from the radiation point of view. J. F. S.

A Formula for the Calculation of the Atomic Weights. ARTHUR W. WARRINGTON (*Chem. News*, 1915, **111**, 110—111).—The approximate atomic weights can be calculated by means of the formula $X = -1 + 2Y + 0{\cdot}008Y^2$, where X is the approximate atomic weight, and Y the number of the element, assuming that there are only eighty-five elements between helium and uranium. G. F. M.

Inorganic Chemistry.

The Question of Unstable Forms of Ice. P. W. BRIDGMAN (*Zeitsch. physikal. Chem.*, 1914, **89**, 252—253).—Polemical; an answer to Tammann's criticism (A., 1914, ii, 633) of the author's original paper (A., 1913, ii, 39), in which it is shown that in all probability two forms of ice II exist. J. F. S.

Sublimation of Iodine in the Laboratory. FRITZ C. KOEHLER (*Chem. Zeit.*, 1915, **39**, 122).—A simple apparatus for the purification of recovered iodine in the laboratory by sublimation consists of a glass funnel in which is placed a tubulated glass globe consisting of two halves ground to fit on one another, such as is used in vacuum distillations. A glass tube, projecting into the middle of the globe and fitted tightly into the tubulure with asbestos, passes downwards through the stem of the funnel and ends in a glass flask having a hole in the base plugged with glass-wool, and resting on a beaker. The impure iodine is placed in the lower half of the glass globe and is warmed by a slow current of steam passing through the funnel. A cake of pure dry sublimate is obtained on the upper half, all the moisture passing through the glass tube into the lower flask and beaker. The apparatus works day and night without attention, and using a globe 15 cm. in diameter 250—300 grams of pure dry iodine were obtained in a few days. G. F. M.

The Action of Carbon Dioxide on Mineral Sulphides. N. COSTEANU (*Ann. Chim.*, 1914, [ix], **2**, 189—210. Compare A., 1913, ii, 694; 1914, ii, 48).—Sulphides which are decomposed by water, such as silicon and boron sulphides, and certain sulphides which are insoluble in water, such as zinc sulphide and cuprous sulphide, when heated in an atmosphere of carbon dioxide, act as reducing agents, carbon monoxide being formed, the metallic sulphide converted into the corresponding oxide, and free sulphur liberated. Certain insoluble sulphides, when heated in carbon dioxide, undergo no chemical change, but behave as though heated in a vacuum, and by this means in some cases the transformation from the amorphous to the crystalline state of the sulphide is carried out at a suitable temperature.

Sulphides soluble in water, such as the alkali sulphides, when heated in carbon dioxide are converted into the corresponding carbonates, carbon monoxide, carbon oxysulphide, and free sulphur being formed at the same time. The free sulphur then reacts with some of the carbonate, giving a mixture of alkali pentasulphide and sulphate, carbon dioxide being regenerated:

$$2Na_2S + 4CO_2 = 2Na_2CO_3 + CO + COS + S.$$
$$4Na_2CO_3 + 16S = 3Na_2S_5 + Na_2SO_4 + 4CO_2.$$

W. G.

Sulphites, Thiosulphates and Polythionates. A. SANDER (*Zeitsch. angew. Chem.*, 1915, **28**, 9—12).—The statement of Feld

(A., 1911, ii, 289, 769), that the reaction between mercuric chloride and polythionates is complete only after prolonged boiling, is incorrect. With sodium tetrathionate the reaction is complete at the ordinary temperature after forty to forty-five minutes, depending on the dilution; fifteen minutes are sufficient when the solutions are boiled. The presence of sodium chloride or of other chlorides retards considerably the velocity of reaction.

The oxidation of sulphurous acid by mercuric chloride takes place in accordance with the equation: $H_2SO_3 + 2HgCl_2 + H_2O = H_2SO_4 + Hg_2Cl_2 + 2HCl$. It is only quantitative, however, when the solution contains not more than 2 grams of sulphur dioxide per litre; with greater concentrations sulphur dioxide escapes unoxidised from the boiling solutions.

When excess of mercuric chloride solution is added to a solution of sodium hydrogen sulphite in the cold, reaction takes place according to the equation: $2NaHSO_3 + 2HgCl_2 = 2ClHg{\cdot}SO_3Na + 2HCl$ (compare Barth, A., 1892, 564), the alkali titre of the reaction mixture corresponding quantitatively with the amount of sodium hydrogen sulphite taken. When sulphurous acid is taken in place of sodium hydrogen sulphite, two mols. of sodium hydroxide for every mol. of sulphurous acid are required to neutralise the reaction mixture, which is also in accordance with the above equation, the sulphurous acid first giving sodium hydrogen sulphite. If the neutralised solution is then boiled, it again becomes acid, reactions taking place according to the equations: $2ClHg{\cdot}SO_3Na + H_2O = Hg_2Cl_2 + Na_2SO_4 + H_2SO_3$ and $H_2SO_3 + 2HgCl_2 + H_2O = H_2SO_4 + Hg_2Cl_2 + 2HCl$. Sulphur dioxide is, however, lost from the solution during boiling, so that the reactions are not suitable for quantitative measurements. Normal sodium sulphite behaves similarly to sodium hydrogen sulphite.

The above reactions can be made use of for the estimation of free sulphurous acid in the presence of sulphuric acid. Titration of the acid mixture with alkali, using methyl-orange as indicator, gives the total acid present, the sulphurous acid being thereby transformed into the hydrogen sulphite, and not the normal sulphite. The addition of excess of mercuric chloride and further titration with alkali then gives the amount of sulphurous acid originally present. Mixtures of sulphurous and hydrochloric acid cannot be so estimated, since the presence of the sodium chloride formed on neutralisation with sodium hydroxide interferes, as already mentioned, with the reaction of the mercuric chloride.

The method given by Feld (A., 1913, ii, 617) for the estimation of mixtures of free sulphurous acid with thiosulphates and polythionates is not trustworthy, since the reaction between manganese sulphide and sulphur dioxide, whereby the latter is fixed, does not take place quantitatively according to the reaction:

$$3SO_2 + 2MnS = 2MnS_2O_3 + S,$$

as given by Feld (compare Henderson and Weiser, A., 1913, ii, 327). The following method gives trustworthy results: 10—20 c.c. of the solution are titrated with iodine, thus giving the total amount of thiosulphate and sulphurous acid present. The sulphuric

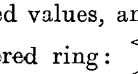
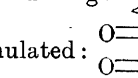
acid thus formed from the sulphurous acid is then titrated with sodium hydroxide, and hence the amounts of thiosulphate and sulphurous acid present can be found. Another 10—20 c.c. of the solution are then neutralised with sodium hydroxide to give sodium hydrogen sulphite; excess of mercuric chloride is then added, the mixture kept for thirty to forty minutes with repeated shaking, and the liberated acid is titrated, after the addition of ammonium chloride, with sodium hydroxide, using methyl-orange as indicator. The amount of liberated acid due to the sulphurous acid and thiosulphate is known from the iodine titration, and hence that due to the polythionate is known, and the amount of polythionate present can be calculated. The reactions of the thiosulphate and polythionates with mercuric chloride take place according to the equations:

$$Na_2S_2O_3 + 2HgCl_2 + H_2O = Na_2SO_4 + Hg_2Cl_2 + 2HCl + S,$$

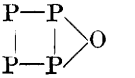
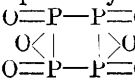
$$Na_2S_nO_6 + 2HgCl_2 + 2H_2O = Na_2SO_4 + Hg_2Cl_2 + H_2SO_4 + 2HCl + (n-2)S.$$

T. S. P.

A Variety of Selenium Particularly Sensitive to Light. Application to the Construction of Selenium Cells for Photometry. Louis Angel (*Bull. Soc. Chim.*, 1915, [iv], **17**, 10—14).—If vitreous selenium melted at 220° is cooled rapidly under pressure it is transformed into a new variety, violet-grey in appearance, formed of slender crystals, very sensitive photoelectrically, but very unstable. The author describes in detail a method of applying this substance in the form of a solid solution in vitreous selenium, in the preparation of a photometric cell, which he has used successfully in the observation of several recent solar eclipses (compare *Compt. rend.*, 1912, **155**, 267). W. G.

Constitution of some Nitrogen and Phosphorus Compounds and the Constitution of Elementary Phosphorus. Gervaise Le Bas (*Chem. News*, 1915, **111**, 113—114).—The author applies the theory of molecular volumes to the determination of ring structure (compare A., 1914, ii, 803). A value of 33·1 is obtained for nitrous oxide at its boiling point by means of Berthelot's formula from the critical data. This shows a contraction of 6·8 compared with the calculated values, and is held to demonstrate the presence of a three-membered ring:  . For similar reasons nitrous anhydride is formulated:  .

In the case of elementary phosphorus there is a contraction of 24·4, which would not be accounted for by a four-membered ring, but agrees with a tetrahedron having a phosphorus atom at each corner, that is, four three-membered rings. Hypophosphorous and phosphorous oxides are formulated respectively as:

 and 

G. F. M.

Vapour Pressure Lines of the System Phosphorus. III. A. SMITS and S. C. BOKHORST (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 962—973. Compare A., 1914, ii, 533; this vol., ii, 49).—Further measurements have been made of the vapour pressure of violet phosphorus. Samples of violet phosphorus were prepared by heating white phosphorus, with or without the addition of iodine, at 375°, 410°, and 550° for prolonged periods. The vapour-pressure curves plotted from the results obtained with the different samples are not identical at temperatures below about 480°, but this was subsequently found to be due to the slowness with which the internal equilibrium is established. At higher temperatures the equilibrium is established much more rapidly. The discontinuity in the vapour-pressure curve, which was found in the earlier experiments, can also be satisfactorily explained in terms of the difference in the speed with which internal equilibrium is established at different temperatures.

By heating in a vacuum at about 360°, an attempt was made to remove the more volatile component and measurements of the vapour pressure of the residue at temperatures below 473° actually gave a curve which is much lower than the curves obtained with the samples of violet phosphorus referred to above. The authors consider that this experiment proves that violet phosphorus consists of at least two allotropic forms (pseudo-components) in internal equilibrium. These components differ greatly in volatility.

In discussing the relation between the various forms of phosphorus, the view is expressed that violet phosphorus represents the unary stable form, white phosphorus the unary meta-stable form, whilst red phosphorus is an intermediate meta-stable form, which is not in internal equilibrium. H. M. D.

The System Phosphorus. A. SMITS and S. C. BOKHORST (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 973—982. Compare preceding abstract).—The vapour-pressure data for solid violet phosphorus yield a straight line when $T \log p$ is plotted as a function of T. This line corresponds with the equation $T \log p = -Q/R + CT$, in which Q is the molecular heat of sublimation and C is a constant. The mean value of Q/R according to the available experimental data is 13050, from which $Q = 25{\cdot}839$ Cal. The heat of vaporisation of liquid violet phosphorus has previously been found to be 9·962 Cal. (compare A., 1914, ii, 534), and by difference 15·877 is obtained as the molecular heat of liquefaction. This extraordinarily high value is supposed to be connected with the chemical change (transformation of one pseudo-component into another) which accompanies the change in state.

According to Giran (A., 1903, ii, 362), the transformation of violet into white phosphorus absorbs 4400 cal. per gram atom, and from this it may be inferred that the heat absorbed in the chemical change accompanying the vaporisation of violet phosphorus is 17·601 Cal. This leaves 8·2 Cal. for the heat absorption, corresponding with the physical change in state.

The critical temperature of liquid violet phosphorus is 695°, and

by extrapolation the critical pressure is found to be 83·56 atm. From the equation $b = T_k/8{\cdot}273p_k$, $b = 0{\cdot}005304$, and when this is compared with the value of b for the atom of phosphorus in phosphine, the ratio of the volumes of the molecule and atom is obtained = 4·26.

When the vapour-pressure data for liquid violet phosphorus are examined in the light of van der Waals' vapour-pressure formula, a difference between the average size of the molecules in the two states of aggregation is also indicated in this way. H. M. D.

Preparation of the Chlorides of Silicon. F. Stanley Kipping (*Chem. News*, 1915, **111**, 135).—The preparation of the chlorides of silicon from ferrosilicon (Martin, T., 1914, **105**, 2836) has been described previously by Warren (A., 1893, ii, 11). H. M. D.

The Fluorides of Silver. A. Guntz and A. A. Guntz, Jun. (*Ann. Chim.*, 1914, [ix], **2**, 101—132).—A more detailed account of work already published (compare A., 1914, ii, 50). W. G.

Magnesium Chloride as a Mineral Former. II. Uranium-Cerium-blue and the Existence of Constitutive Colouring. Magnesia-red and Magnesia-green. K. A. Hofmann and Kurt Höschele (*Ber.*, 1915, **48**, 20—28. Compare A., 1914, ii, 204).—In an earlier paper (A., 1914, ii, 204) attention has been drawn to the application of anhydrous magnesium chloride as a convenient solvent for the crystallisation of metallic oxides.

It is now found that uranium oxide resembles praseodymium oxide in crystallising with cerium oxide, the product having a deep blue colour. The coloured substance is produced by heating a dry mixture of cerium and uranyl sulphates with excess of magnesium chloride in a covered crucible for fifteen hours. The resulting deep blue cubic crystals can be separated from the accompanying magnesia by their relative stability towards dilute acids. The composition of this uranium–cerium-blue varies slightly, but agrees approximately with that of a compound of uranium dioxide with a bimolecular proportion of cerium dioxide.

Uranium dioxide itself can be obtained in a crystalline condition by fusing sodium uranate with magnesium chloride in an analogous manner.

A similar deep blue compound of uranium and cerium dioxides can also be obtained by precipitating an aqueous solution of uranyl and cerous nitrates with excess of ammonium hydroxide or dilute potassium hydroxide solution; the precipitate is at first yellow, but soon changes to a denser blue solid. This result is attributed to a reduction by the primarily produced cerous hydroxide, followed by combination of the resulting dioxides. The blue compound can, in this case, be isolated by treatment with ammonium hydrogen carbonate solution, which removes excessive uranium dioxide as uranium ammonium carbonate, but if this process is too prolonged the blue compound undergoes decomposition with formation of doubly refracting crystals of *cerous ammonium carbonate*,

$$Ce_2(CO_3)_3,(NH_4)_2CO_3,6H_2O.$$

It was not found possible to obtain analogous results by wet methods with other metals in place of uranium. Ammonium vanadate and cerium nitrate on treatment with ammonium hydroxide gave a dirty-brown precipitate, or on mixing in suitable proportions without the ammonia yielded amber-yellow, rhombic plates of complex composition. Ammonium molybdate and cerium nitrate in aqueous solution gave a complex ammonium cerimolybdate, $Ce_2O_3,10MoO_3,2NH_3,8H_2O$.

The colour of uranium–cerium blue is explained in the same manner as that of the ferriferrocyanides (Hofmann and Resenscheck, A., 1906, i, 75), namely, by an oscillatory variation in the valency of the two central atoms.

By heating cobalt sulphate with magnesium chloride in a porcelain crucible, octahedral crystals of "magnesia-red" can be obtained more easily than by the earlier process (Hedvall, A., 1914, ii, 373); the addition of magnesia is not necessary, as it is produced during the heating. By a similar process nickel sulphate gives rise to green, octahedral crystals ("magnesia-green"). These crystals are mixed crystals of the two oxides. In experiments with manganese, complications arise on account of atmospheric oxidation.

Attention is drawn to the ease with which, on fusion with magnesium chloride, many basic oxides react with formation of a chloride which sublimes away, leaving a residue of magnesium oxide. D. F. T.

Action of Lead, Copper, Tin, Nickel, Zinc, and Aluminium on Water. W. P. Jorissen (*Chem. News*, 1915, **111**, 56—58, 67—70, 78—80, 91—92, 102).—A report on recent investigations on the corrosive action of pure and natural waters on the above metals read before the Chemical Section of the 11th Inter. Pharm. Conf. As regards his own conclusions, the author considers that it is not possible to predict whether a special kind of drinking water, brought into contact with lead or zinc, will only dissolve quantities below a certain limit, but that a special experiment must be made in each case with the conditions imitated as nearly as possible. There is little danger of much corrosion of tin by drinking water. G. F. M.

The Nature of Subsidiary Valencies. VIII. Stability of the Metal Ammonias of Chlorates, Bromates, and Iodates. Thermal Dissociation and Explosion. Fritz Ephraim and Adolph Jahnsen (*Ber.*, 1915, **48**, 41—56. Compare Ephraim, A., 1914, ii, 179, 827; 1913, ii, 129, 130, 496, 578, 677, 1061; Ephraim and Linn, A., 1914, i, 17).—The metal-ammonias of the chlorates, bromates, and iodates are easily obtainable, but in the case of the derivatives of the two former, investigation of the dissociation curves is limited by the explosive nature of the compounds at higher temperatures. It is of interest that the explosion temperature of the metal-ammonias derived from the chlorates of the metals zinc, nickel, and copper coincides approximately with the temperature

at which the dissociation pressure becomes equal to the atmospheric pressure, and that this may not be a chance coincidence is confirmed by the fact that under increased pressure the explosion temperature is raised. With the metal-ammonias derived from the bromates, on the other hand, no marked difference is observable between the explosion temperature under ordinary atmospheric pressure and in sealed vessels. In the case of the metal-ammonias of the iodates of copper, nickel, zinc, and cadmium, dissociation occurs at relatively low temperatures, although explosions cannot be produced in the open atmosphere, but only in sealed vessels, the requisite temperatures being between 210° and 219°. The metal-ammonias of the chlorates and bromates, in addition to exploding on heating, can also be exploded by shock.

The constant product, $\sqrt[3]{v}.\sqrt[3]{T}$, where v is the atomic volume of the metal, and T the absolute dissociation temperature, is again found to give a slightly high value for the nickel compounds, and a decidedly high one for those of cadmium; these discrepancies may be due to an alteration in the atomic volume of the metals on combination, a view which receives a certain amount of support from a comparison of the molecular volumes of the compounds.

The following compounds are described: *Coppertetrammine chlorate*, deep blue needles; *copperhexammine chlorate*, deep blue; *nickelhexammine chlorate*, blue crystals, m. p. near 180°; *zinctetrammine chlorate*, colourless crystals; *zinchexammine chlorate*; *cadmiumhexammine chlorate*, colourless crystals; *cadmiumtetrammine chlorate*; *cobalthexammine and cobalt-tetrammine chlorates* were unstable, as also was a *manganeseammine chlorate* of unknown ammonia content. There were also obtained: Coppertetrammine bromate, blue needles; *nickelhexammine bromate*, violet, crystalline powder; *zinctetrammine bromate*, crystalline powder; *cadmiumtetrammine bromate*, crystalline powder; anhydrous *copper iodate* (that described by Ditte, A., 1892, 1388 is the monohydrate), brown; *coppertetrammine iodate dihydrate*, blue prisms; *copperpentammine iodate*; *nickelpentammine iodate*, violet; *nickelpentammine iodate trihydrate*, reddish-violet crystals; *zinctetrammine iodate*, colourless needles; *cadmiumtetrammine iodate*, microscopic prisms. D. F. T.

Action of Ammonium Salts on Mercuric Iodide. I. Icilio Guareschi (*Atti R. Accad. Sci. Torino*, 1914–1915, **50**, 231—236).—When a mixture of mercuric iodide with a little ammonium bromide is heated in a long, narrow tube of hard glass, violet iodine vapours are evolved, the aqueous extract of the cold mass giving an intense coloration with starch solution. The reaction, which is shown clearly by as little as 0·0001 gram of mercuric iodide, is due to the formation and subsequent decomposition of ammonium iodide; it takes place also in solution. The presence of mercuric chloride or bromide, or lead bromide hinders the reaction, which is, however, not affected by an excess of potassium bromide. When heated with ammonium chloride, mercuric iodide yields scarcely any iodine, whilst with ammonium sulphate or nitrate much iodine is liber-

ated, but the cold mass gives no coloration with starch solution. The reaction is given also by ammonium dichromate. Mercurous iodide and ammonium bromide yield no iodine, the reactions occurring being expressed by the equations: $Hg_2I_2+2NH_4Br=HgBr_2+Hg+2NH_4I$, $2NH_4I=2NH_3+H_2+I_2$, and $Hg+I_2=HgI_2$. The presence of mercurous iodide or bromide also prevents the reaction with mercuric iodide.

Mercuric iodide is readily soluble in cold ammonium bromide solution, and if the dry residue of the liquid is heated, iodine vapour is immediately evolved. This reaction allows of the separation and characterisation of mercuric iodide when mixed with large proportions of many other insoluble red compounds; thus, mercuric sulphide (cinnabar) containing only 0·1% of the iodide responds to the test. This is not the case, however, when the mixture of mercuric sulphide and iodide is heated with water and ammonium bromide, owing to the formation of ammonium sulphide, sulphur, etc.

When a mixture of a little mercuric iodide with much manganese dioxide is slowly heated, iodine vapour is liberated at first, but the mercuric iodide subsequently sublimes; with rapid heating, scarcely any iodine is set free. Addition of ammonium bromide to this mixture results in the copious evolution of iodine vapour.

If a mixture of mercuric iodide and antimony sulphide is heated with ammonium bromide, ammonia is liberated in large quantity, and a sublimate forms, but no iodine can be detected. When this mixture is treated with aqueous ammonium bromide and the dried crystalline residue of the solution heated, faintly violet vapours form, but no reaction is given with starch; the presence of an iodide is, however, shown by addition of chlorine water. T. H. P.

Sublimation and Dissociation of Aluminium Nitride. Fr. Fichter and Gust. Oesterheld (*Zeitsch. Elektrochem.*, 1915, **21**, 50—54).—Aluminium nitride is usually obtained as a grey, amorphous mass, but some specimens contain rosettes of colourless, hexagonal needles. The present paper gives the results of an attempt to explain the origin of the crystals. The results of the experiments show that the crystals are the result of sublimation. Weighed quantities of aluminium nitride were heated in a tungsten-tube electric furnace to various temperatures in an atmosphere of nitrogen, and the amount of sublimation noted, as well as the nature of the sublimate. Experiments of a similar nature were also carried out in a carbon tube. It is shown that aluminium nitride begins to sublime in a tungsten tube at $1870°\pm20°$ when under a pressure of 14 mm. of nitrogen, and that at $1890°\pm20°$ the sublimation is very rapid under the same conditions. The sublimation is accompanied by a partial dissociation of the aluminium nitride into its elements $2AlN \rightleftarrows 2Al+N_2$; the distillate settles as a crystalline deposit, which contains considerable quantities of metallic aluminium. The dissociation is more complete the lower the pressure of nitrogen, and it is still more complete when aluminium nitride is heated in hydrogen at 2 mm. pressure. When

higher pressures of nitrogen are used the tungsten tube is attacked, and consequently no trustworthy results could be obtained in this way. Experiments in carbon or graphite tubes filled with nitrogen at atmospheric pressure show that sublimation occurs without the formation of metallic aluminium, but the sublimate is contaminated with aluminium carbide and carbon. When aluminium carbide is heated quickly to 2000°, it partly dissociates, and leaves a residue of graphite. When an arc is struck between aluminium electrodes in nitrogen, a fine, grey sublimate, of aluminium nitride which contains metallic aluminium, is formed. This product can be freed from aluminium by distillation of the aluminium at 1840° in hydrogen of low pressure. J. F. S.

The Reactions between Ferrous Oxide and Carbon, and between Carbon Monoxide and Iron. V. FALCKE (*Zeitsch. Elektrochem.*, 1915, **21**, 37—50. Compare A., 1913, ii, 327).—Using the same apparatus as previously employed, the author has studied the above-mentioned reactions at temperatures from 600° upward, and has also examined the gaseous products obtained when the reaction mixtures were dissolved in hydrochloric acid. In the experiments, three varieties of graphite and five varieties of amorphous carbon were used. These were subjected to prolonged purification, and were then analysed and their densities obtained. The solid mixtures examined were introduced into the apparatus in the form of compressed pellets. It is shown that below 650° none of the highly-purified forms of carbon react with ferrous oxide, and above this temperature the various varieties behave differently, but fall into three groups. Sugar charcoal and charcoal obtained by the action of carbon monoxide on sodium are very inert, and a vigorous reaction does not take place until a temperature of 800° has been reached, and in these cases an equilibrium pressure was not obtained. Charcoal obtained by burning acetylene in chlorine, and charcoal from petroleum reacted more easily, showing a vigorous action at 650°. Whether the difference in the reactions is due to different modifications of carbon, or whether it is due to catalytic influences, cannot be decided from the experiments. The three forms of graphite react similarly, and the great capacity of graphite for this reaction is due in the author's opinion to the fact that the reactions commence slowly, and increase gradually to a definite limiting value, after which they proceed at a constant rate until the reaction is complete, which is taken to imply that a contact reaction occurs in the solid mixture which precedes the evolution of gas, and which is probably one of solution or direct combination. The reaction products of the action of carbon on ferrous oxide contained pure iron, but no hydrocarbons were obtained when the solid product was dissolved in hydrochloric acid. In the case of the action of carbon monoxide on iron, it was found that when carbon monoxide was led into the apparatus until a considerable amount had been absorbed by the iron and the equilibrium pressure set up at 600°, the product on solution in hydrochloric acid gave large volumes of saturated hydrocarbons, chiefly ethane, but no

solid carbon was left. On the other hand, when iron was heated in a stream of carbon monoxide, or when iron was allowed to absorb large quantities of carbon monoxide and then heated in a vacuum, and the product dissolved in hydrochloric acid, no hydrocarbons were evolved, but a residue of carbon remained behind. The work and views of Schenck and his collaborators (A., 1905, ii, 519; 1907, ii, 470) are criticised. J. F. S.

Magnetic Oxide of Chromium. TAKÉ SONÉ and TORAJIRÔ ISHIWARA (*Sci. Rep. Tôhoku Imp. Univ.*, 1914, **3**, 271—275).—In a previous paper (this vol., ii, 8) the magnetic susceptibility of the oxides obtained by heating chromic anhydride was investigated. The magnetic behaviour of the oxide obtained from chromyl chloride (Wöhler, *Annalen*, 1859, **111**, 117) has now been examined. The chromyl chloride vapour is passed through a long glass tube heated at 400°, whereby a grey or black deposit is obtained. Samples from different parts of the tube were examined separately, and found to differ considerably in respect of their magnetic susceptibility. Chemical analysis of the samples showed a corresponding variation in the composition, the susceptibility increasing with the percentage content of the oxide, $Cr_5O_9(2Cr_2O_3,CrO_3)$. One of the samples examined contained as much as 96% of this magnetic oxide.

Different samples were also used in the determination of the critical temperature, giving the same result, ±150°. This is about 30° higher than that recorded by Shukov (A., 1908, ii, 699).

H. M. D.

Bismuth Suboxide. W. HERZ [with A. GUTTMANN] (*Zeitsch. anal. Chem.*, 1915, **54**, 103. Compare A., 1907, ii, 274).—Bismuth suboxide prepared according to Schneider's method (A., 1899, ii, 227) had D 7·9, and its composition corresponded with the formula BiO; if the substance had been a mixture of Bi and Bi_2O_3, it would have had D 8·9. As prepared by Tanatar's method (A., 1901, ii, 553), the suboxide obtained had D 7·6, owing to the presence of 1% of other substances; it contained 91·8% of bismuth.

W. P. S.

Experiments with Colloidal Gold and Silver. EDSON S. BASTIN (*J. Washington Acad. Sci.*, 1915, **5**, 64—71).—The results obtained in the precipitation of gold and silver from solutions of their salts by the action of minerals are described. The supposition that the brown gold obtained by the action of chalcocite is colloidal in character has been confirmed by comparative observations on the deposition in presence and absence of gelatin. Minerals which give rise to dull brown or black gold are favourable to the formation of colloidal solutions, and the opposite holds for minerals which yield lustrous yellow deposits. It has been found that the colloidal gold originates on the surface of the mineral, and diffuses slowly into the solution.

The observations on silver solutions are similar in character. In

presence of gelatin, a part of the silver which would otherwise be precipitated by minerals is transformed into colloidal silver. Silica sols have much the same effect as gelatin. H. M. D.

Catalytic Actions of Colloidal Metals of the Platinum Group. XI. Reduction of Molybdic Acid. C. PAAL and HANS BÜTTNER (*Ber.*, 1915, **48**, 220—223).—It was recently stated that aqueous solutions of ammonium molybdate are reduced by hydrogen in presence of colloidal palladium to molybdenum tetrahydroxide (A., 1914, ii, 642). The experiments have been repeated with a more active preparation of the catalyst. The reduction to the tetrahydroxide is completed at ordinary temperatures, but the absorption of hydrogen begins anew if the mixture is warmed to 50—60° and a slight pressure is used, and then the insoluble molybdenum trihydroxide is formed as a black sludge, according to the equation:

$$(NH_4)_6Mo_7O_{24},4H_2O + 21H = 7Mo(OH)_3 + 6NH_3 + 7H_2O.$$

J. C. W.

Mineralogical Chemistry.

The Mineral Empressite. W. M. Bradley (*Amer. J. Sci.*, 1915, [iv], **39**, 223).—The following mean of two new analyses made by E. J. Dittus on empressite (A., 1914, ii, 737) from the Kerber Creek district, Colorado, confirms the formula AgTe:

Ag.	Te.	Fe.	CaO.	Insol.	Total.
43·69	53·83	2·16	trace	0·33	100·01

L. J. S.

Tetranickel Triarsenide [Maucherite] as a Silver Precipitant. Chase Palmer (*Econ. Geol.*, 1914, **9**, 664—674).—Maucherite (A., 1913, ii, 516) from Eisleben and Mansfeld in Thuringia, and temiskamite from Elk Lake, Ontario (A., 1914, ii, 210), are completely decomposed by a solution of silver sulphate, the nickel and arsenic passing into solution in the ratio given by the formula Ni_4As_3. One molecule of this compound deposits seventeen atoms of metallic silver in the form of arborescent crystals. It is suggested that temiskamite is identical with the earlier-described maucherite, and that the true formula is Ni_4As_3, rather than Ni_3As_2. Samples of the mineral from these three localities (containing 98·62, 95·84, and 92·76% Ni_4As_3 respectively) had D^{25} 7·81, 7·80, and 7·73 respectively. Niccolite (NiAs) is also capable of depositing silver from a solution of a silver salt, but smaltite ($CoAs_2$), cobaltite (CoAsS), and arsenopyrite (FeAsS) are strongly resistant. These reactions have a bearing on the enrichment in silver of mineral veins containing nickel arsenides. L. J. S.

Crystallisation-Differentiation in Silicate Liquids. N. L. BOWEN (*Amer. J. Sci.*, 1915, [iv], **39**, 175—191).—Experiments were made with the materials previously used in the examination of the ternary system diopside–forsterite–silica (A., 1914, ii, 772). The materials were kept for various periods at temperatures at which crystals and liquid exist together, and the mass was then suddenly cooled. When olivine or pyroxene crystals have separated, the glass is clear in the upper portions, cloudy in the middle portions, and opaque at the bottom, and thin sections under the microscope showed the presence of increasing numbers of crystals towards the bottom of the mass. On the other hand, crystals of tridymite were found to have floated to the surface. The rate of sinking of the crystals affords a rough estimate of the viscosity of the fusions, and these show a progressive increase of viscosity with increase of silica. These results are discussed in relation to the differentiation of rock magmas. Evidence of the sinking of olivine crystals is shown in the Palisade diabase sill in New Jersey.

L. J. S.

Analytical Chemistry.

Electrometric Titrations. HENRY ZIEGEL (*Trans. Amer. Electrochem. Soc.*, 1914, **26**, 91—97).—When a ferrous solution in sulphuric acid is titrated by a standard solution of potassium dichromate, there is a sudden change in the oxidation potential of the solution at the point where the oxidation is complete amounting to rather more than 0·2 volt. This fact is made use of by the author in devising an automatic method of estimating iron by means of potassium dichromate. The iron solution is placed in a beaker, in which a platinum-plated metal rod, fitted at its end with a platinum plate, is suspended from a small electric motor. This rod acts when in motion as a stirrer and as an oxygen electrode. A calomel electrode furnishes the other half of the cell. The two electrodes are connected in the usual way with a bridge wire, and also with a number 30 Weston relay. The relay operates a lever, which as soon as the current is switched on opens the burette tap and when the sudden change in potential occurs closes it again, thus making the titration automatic. A series of titrations carried out by this method and also by the usual "outside indicator" method are given; the two series agree closely enough to show that the automatic process is trustworthy. J. F. S.

Further Use of the Boric Acid Method. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1915, **28**, 48).—The method previously recommended by the author for absorbing ammonia by means of boric acid, the ammonia then being titrated directly with hydrochloric acid (A., 1913, ii, 527), can be used also in the estimation of fatty

amines, for example, methylamine and trimethylamine. By an extension of the method, pharmaceutical preparations such as lithium carbonate and basic magnesium carbonate can be analysed.

0·1 Gram of lithium carbonate and 1 gram of boric acid are heated with 10 c.c. of water until the lithium salt has dissolved completely, and all the carbon dioxide has been expelled. The solution is then titrated with $N/10$-hydrochloric acid, using methyl-orange as indicator. If the lithium carbonate contains sodium carbonate, 0·122 gram of the mixture, dried at 160—180°, is treated in the same way. Pure lithium carbonate would require 33·03 c.c. of $N/10$-hydrochloric acid for neutralisation; every 0·1 c.c. less of acid required corresponds with 1% of sodium carbonate.

Basic magnesium carbonate is treated similarly, taking 2 grams of boric acid and 20—30 c.c. of water for 0·1 gram of the carbonate.

In estimating the alkalinity of waters rich in carbonic acid by titration with acid, the end-point is not sharp. If, however, 1—2 grams of pure boric acid are boiled with 100 c.c. of the water for a few minutes, and the water then cooled, the end-point is quite sharp.

The boric acid method can also be used for the estimation of a few of the alkaloids, for example, atropine and codeine, but not for all, for example, quinine. T. S. P.

General Principles Governing the Complete Analysis of Minerals and Ores. W. R. Schoeller (*Analyst*, 1915, **40**, 90—106).—A systematic outline is given of the course to be adopted in the analysis of inorganic and metallurgical substances. The paper is arranged under the following headings: (1) Methods for estimating elements; (2) separation of elements; (3) other methods of separation; (4) typical minerals; (5) preliminary qualitative examination; (6) separation into insoluble residue and soluble fraction; (7) organic matter; (8) estimation of heavy metals; (9) separate estimation of certain constituents; (10) oxidised minerals; (11) mixed oxide and sulphide ores; (12) estimations by difference; loss on ignition; (13) choice of methods; purity of reagents; (14) accuracy; "traces"; statement of results; (15) bibliography. Tables are given showing the methods suitable for the separation and estimation of various metals when present in large or small quantities. W. P. S.

Water Analysis. L. W. Winkler (*Zeitsch. angew. Chem.*, 1915, **28**, 22—23).—The presence of active chlorine in drinking water which has been treated with bleaching powder for the destruction of bacteria is best tested for as follows: To 250 c.c. of the water are added 1—2 drops of a very dilute methyl-orange solution (1:5000) and 2—3 c.c. of 10% hydrochloric acid. If hypochlorites are present the methyl-orange is immediately, or almost immediately, decolorised, whereas a blank test on pure water remains coloured. Nitrites do not affect the test, unless present in abnormally large quantity, and even then the decolorisation takes upwards of an hour. Hydrogen peroxide also has no effect, but

ozone decolorises the methyl-orange, although more slowly than active chlorine. The presence of ozone can be detected, however, by its characteristic odour. 0·1 Mg. of active chlorine per litre can thus be detected. With methyl-red as indicator the test is sensitive to 0·02 mg. of active chlorine. 0·01 Gram methyl-red is dissolved in 1 c.c. of $N/10$-sodium hydroxide, and the solution diluted to 100 c.c.; 1 drop of this solution is used to 500 c.c. of water.

Water containing manganese should first be cleared with alum before the test is carried out.

The quantitative estimation of the active chlorine is carried out by the addition of pure potassium iodide (0·2 gram to 100 c.c. of water), 1 c.c. of starch solution, 2—3 c.c. of 25% phosphoric acid, and titration of the liberated iodine with $N/200$-thiosulphate.

The above tests can be readily modified for the detection of manganese in water. After the addition of the methyl-orange solution (1 drop) to the water (250 c.c.), 1—2 c.c. of 10% sodium hydroxide are added; after a few minutes 5 c.c. of 10% hydrochloric acid are added. If manganese is present, decolorisation takes place immediately or in one to two minutes. A blank test on pure water should be performed at the same time. The test is useful when collecting water at its source, and is sensitive to 0·1 mg. of manganese per litre. It is not affected by the presence of iron, but the sensitiveness is much reduced when nitrites or appreciable quantities of organic matter are present. It can then be made more sensitive by again making the water alkaline and acidifying after one to two minutes. In waters containing hydrogen sulphide the test cannot be applied.

The amount of phosphoric acid present in drinking and ordinary waters is generally extremely small. The author gives full details, which are lengthy and complicated, of the methods which may be used for the detection and estimation of the phosphoric acid. The principle of the methods is to precipitate the phosphoric acid as ferric phosphate by the addition of a solution of ferric chloride and alum. The ferric phosphate is then transformed into phosphomolybdate, the amount of which can be estimated either colorimetrically or gravimetrically. T. S. P.

The Quantity of Bromides in Table Salts. L. Chelle (*Ann. Chim. anal.*, 1915, **20**, 32—34; from *Bull. Soc. Pharm. Bordeaux*, 1914, 19).—Bromides are present in all (French) table salts; the salt prepared from sea-salt contains from 0·015 to 0·058% of bromine, that from rock salt from 0·008 to 0·020%, whilst a salt obtained by the interaction of potassium chloride and sodium nitrate (Chile saltpetre) contains from 0·070 to 0·140%. The ratio, 1000Br/Cl, is always less than 1·0 in the case of salt prepared from sea-salt and rock salt, but exceeds 1·5 with salt obtained from potassium chloride and sodium nitrate; this ratio, in conjunction with a test for nitrates, will indicate the origin of a sample of salt. The author is of opinion that almost all of the bromide found in normal urine may have its source in the table salt consumed. W. P. S.

Methods of Analysis of Sulphur. M. G. Levi (*Ann. Chim. Applicata*, 1915, i, 9—31).—The author's investigations of the various methods which have been proposed for the analysis of crude sulphur give the following results:

Estimation of the sulphur by the Carius' method always results in a small positive error, which is, however, much less than that found by Anelli (A., 1911, ii, 533). The method in which the sulphur is burnt in a current of oxygen and the gaseous products collected in hydrogen peroxide solution (compare Bennett, *Rass. Min.*, 1911, **34**, 149) is exact, and easily carried out with moderately pure sulphurs, but is less certain and more tedious in the case of sulphur containing an appreciable proportion of bitumen. Oxidation by means of nitric acid mixed with either bromine or potassium bromide (compare Berger, A., 1907, ii, 129) gives exact results when use is made of suitable apparatus and conditions, which are described in detail by the author.

Fresenius and Beck's method (*Zeitsch. anal. Chem.*, 1903, **42**, 21) is carried out as follows: Ten grams of the sulphur are placed in an uncovered 100 c.c. porcelain crucible immersed to its rim in a sand-bath, the temperature of which is raised to just above 200°. The residue from this heating represents bitumen + ash, and the latter is then estimated alone by igniting the crucible. This method gives accurate results, and, owing to the large quantity of sulphur taken, the errors of sampling are greatly diminished.

When sulphur of inferior quality is to be examined, the so-called "mineral residue" should be removed by careful extraction with carbon disulphide, the sulphur being estimated in the extract.

T. H. P.

Estimation of Sulphur in Organic Substances. A. Krieger (*Chem. Zeit.*, 1915, **39**, 22—23).—Eschka's method for the estimation of sulphur in organic substances, particularly for coal and coke, is not satisfactory, the most important reasons being that the operations require too long, that the reagents used, and the atmosphere in which it is performed are rarely themselves free from sulphur, and that silicic acid from the coal is often deposited along with the barium sulphate. The various modifications which have since been suggested mostly require special apparatus, and a variation of Hollinger and Dennstedt's method is recommended (A., 1909, ii, 343, 435). From 0·5 to 1·0 gram of substance are weighed into a combustion boat, before which is placed a copper spiral to warm the oxygen in which the combustion is carried out, so as to avoid direct heating as far as possible. On the other side of the boat the combustion tube is filled for a length of 10 cm. with fragments of silica. The combustion is carried out in the usual way, and the sulphuric acid is absorbed in $N/5$-sodium hydroxide and determined volumetrically by back-titration with hydrochloric acid. The amount of sulphur remaining in the ash is only about 0·05%. For the determination of sulphur in plants and food-stuffs the following process is recommended in preference to the oxygen combustion. Four grams are heated with 20 c.c. of nitric acid

(D 1·48) in a Kjeldahl flask until a clear liquid is obtained. After dilution and filtration the sulphuric acid is precipitated as barium sulphate. Silica, if present, does not go into solution, and hence evaporation of the nitric acid solution is unnecessary. The author claims for this nitric acid method a very general applicability to organic substances, but it does not give satisfactory results with coal or coke. G. F. M.

Comparative Study of Methods for the Estimation of Sulphur in Peptone. HARRY W. REDFIELD and CLARENCE HUCKLE (*J. Amer. Chem. Soc.*, 1915, **37**, 607—611).—The various methods which have been recommended for the estimation of sulphur in organic compounds have been compared experimentally, Witte peptone being used as the sulphur-containing material.

It was found that of all those tried, the Liebig-Koch method gave the highest and most consistent results. During the preliminary treatment with nitric acid, no sulphur was lost by volatilisation, and the continuation of the digestion with nitric acid for more than two hours did not have any effect.

Of the methods examined for the estimation of only a part of the sulphur, the best results were obtained by the Schultz method described by Osborne (A., 1902, i, 251) for loosely-bound sulphur, and by digestion with nitric acid and potassium chlorate for easily oxidised sulphur. E. G.

Estimations of Sulphur in the Culture Medium for the Detection of the Bacteria Producing Hydrogen Sulphide. HARRY W. REDFIELD and CLARENCE HUCKLE (*J. Amer. Chem. Soc.*, 1915, **37**, 612—623).—This investigation was carried out by the methods of estimating sulphur in peptone which have already been found the most suitable for the purpose (preceding abstract).

A culture medium containing 3% of Witte peptone and 0·75% of potassium chloride was inoculated with artificial sewage. It was found that the bacteria were most active, and produced the largest quantity of hydrogen sulphide when supplied most freely with air. From 25% to 30% of the total sulphur was converted into hydrogen sulphide when the cultures were incubated for forty-eight hours whilst sterile air was passed over them, and from 50% to 60% when incubated for seventy-two hours. In media made from that portion of the peptone which is soluble in alcohol, much less sulphur-containing material was broken down, and very much less hydrogen sulphide was produced than in media made from the insoluble portion of the peptone. In both of these media very much less sulphur-containing material was broken down, and very much less hydrogen sulphide was produced than in the simple peptone medium.

A larger percentage of sulphur-containing material than of total peptone was broken down, the ratio being about 3 : 1. The ratio of easily oxidised sulphur to that of total sulphur converted into hydrogen sulphide by the bacteria was about 4 : 3, that of loosely-bound sulphur to total sulphur converted into hydrogen sulphide

was about 3:2, and that of loosely-bound sulphur to easily oxidised sulphur converted into hydrogen sulphide by the bacteria was about 10:9. There was about twice as much easily oxidised sulphur as loosely-bound sulphur present both before and after the action of the bacteria on the medium. E. G.

Reaction for the Identification of Traces of Selenium. G. DENIGÈS (*Ann. Chim. anal.*, 1915, **20**, 59—61).—A small quantity of the selenium is heated with a few drops of nitric acid, and to the mixture is added its own volume of water and of mercurous nitrate solution containing 10% of nitric acid. A crystalline precipitate of mercurous selenite is obtained either at once or after cooling; the crystals exhibit a characteristic shape when examined microscopically. In dealing with very small quantities of selenium the test may be carried out on a microscopic slide. W. P. S.

Reactions of Selenic and Telluric Acids and their Salts. G. DENIGÈS (*Ann. Chim. anal.*, 1915, **20**, 57—59).—The reagent employed is prepared by dissolving 10 grams of mercurous nitrate in a mixture of 10 c.c. of nitric acid (D 1·39) and 100 c.c. of water. When a solution of selenic acid or its salts is mixed with one-half its volume of the reagent, a precipitate of mercurous selenate is formed; this precipitate rapidly becomes crystalline, and the crystals are seen under the microscope to consist of small clusters. When the concentration of the selenic acid exceeds 1% the needles appear as an aggregate of smaller crystals. Selenious acid and its salts yield a precipitate consisting of long needles, the reaction being obtained with 0·1% solutions of the acid. Under similar conditions, telluric acid and tellurates yield a yellow, crystalline precipitate of mercurous tellurate; these crystals appear either as triclinic plates or, more frequently, speroidal masses. W. P. S.

Estimation of Nitrogen in Coke. B. M. MARGOSCHES (*Chem. Zeit.*, 1915, **39**, 167—168).—A discussion of the various modifications of the Kjeldahl method. The difficulty of obtaining the total quantity of nitrogen is pointed out; the method usually tends to give lower results than are found by the combustion process. W. P. S.

Comparison of Various Modifications of the Kjeldahl Method with the Dumas Method of Estimating Nitrogen in Coal, with Notes on Errors in the Dumas Method due to Nitrogen evolved from the Copper Oxide. ARNO C. FIELDNER and CARL A. TAYLOR (*J. Ind. Eng. Chem.*, 1915, **7**, 106—112).—Comparative estimations of nitrogen in coals by various modifications of the Kjeldahl method showed that the highest and most concordant results in the shortest time of digestion were obtained by the Kjeldahl-Gunning method, using both mercury and potassium sulphate, as proposed by Dyer (T., 1895, **67**, 811). Mercury was more effective than copper sulphate as a catalyst, and for raising the boiling point of the mixture potassium sulphate

was found to be better than phosphoric oxide. Modifications of the method for the estimation of nitrates or nitro-compounds did not give results appreciably different from those obtained by the Kjeldahl-Gunning method. The addition of permanganate at the end of the digestion did not cause loss of nitrogen. To obtain the maximum yield of nitrogen, it was found necessary to continue the digestion for two hours after the mixture had become colourless. The greatest difference in the average values found by the Kjeldahl-Gunning method and the Dumas gas-volumetric method was 0·1%; the mean difference was 0·05%. Errors in the Dumas method due to nitrogen contained in the copper oxide may be minimised by previously heating the oxide for several hours under reduced pressure and cooling it in an atmosphere of carbon dioxide; it is preferable to use "wire form" copper oxide powdered to pass a 40-mesh sieve and remain on a 100-mesh sieve.

W. P. S.

Methods of Estimating Ammonia in Soils. B. Tarasov (*Bied. Zentr.*, 1915, **44**, 4—6; from *J. exper. Landw.*, 1914, 136).—The results obtained by Boussingault's method are generally too high. As regards Schloesing's method it was found that one treatment with hydrochloric acid does not extract the whole of the ammonia, and that ammonia may be produced from the organic compounds present. With Prianischnikov's method, high results, as compared with Schloesing's method, were obtained with black soils, and low results with loams. N. H. J. M.

An Improved Method for the Estimation of Inorganic Phosphoric Acid in Certain Tissues and Food Products. Robert M. Chapin and Wilmer C. Powick (*J. Biol. Chem.*, 1915, **20**, 97—114).—Organic matter is precipitated by picric acid, and the inorganic phosphorus estimated in an aliquot portion of the filtrate. Examples are given to show that accuracy was obtained. In eggs, as deterioration advances, the ratio of inorganic phosphorus rises.

W. D. H.

Estimation and Separation of Arsenic by Simply Boiling its Hydrochloric Acid Solution in the Presence of Hydrazine Salts and Potassium Bromide. P. Jannasch and T. Seidel (*J. pr. Chem.*, 1915, [ii], **91**, 133—173).—Arsenic may be quantitively volatilised and separated from antimony, mercury, copper, silver, lead, gold, bismuth, cadmium, tin, and other metals, and also from phosphoric, vanadic, and molybdic acids, by distilling its hydrochloric acid solution with potassium bromide and hydrazine sulphate or chloride.

The substance for analysis, which should not contain more arsenic than corresponds with 0·3 gram As_2O_3, is boiled with 100—120 c.c. of hydrochloric acid (D=1·19), 1 gram of potassium bromide, and 3 grams of hydrazine salt until the volume of the residual liquid measures 25—30 c.c., the distillate being collected in 300 c.c. of water; the arsenic is readily estimated in the distillate by titration

with potassium bromate until the red colour produced by the addition of two drops of methyl-orange is just discharged (compare Györy, A., 1893, ii, 554). If more arsenic is present than corresponds with 0·3 gram As_2O_3, a second distillation is necessary. This method of removing arsenic has the advantage that the metals in the residue may be readily estimated, the hydrazine salts being destroyed by evaporation with nitric acid. Full details of the estimation of the metals enumerated above are given, together with several examples of the application of the method to the estimation of arsenic in minerals. F. B.

Estimation of Arsenic in Iron, Steel, and Ores. A. Kleine (*Chem. Zeit.*, 1915, **39**, 43).—The apparatus required consists of a 300 c.c. conical flask fitted with a long, perpendicular glass tube leading to the upper end of a vertical condenser, to the lower end of which is connected a second flask to collect the distillate. Ten grams of the sample are dissolved in 120 c.c. nitric acid (D 1·2), and the solution is evaporated to dryness and heated until brown fumes are no longer evolved. The residue, dissolved in slightly warm concentrated hydrochloric acid, is then distilled from the conical flask after the addition of 1 gram of potassium bromide and 3 grams of hydrazine sulphate. Arsenious chloride distils over with water and hydrochloric acid, and is collected, the mechanical carrying over of iron being prevented by the length of the connecting tubing. In the distillate the arsenic is determined by precipitating as sulphide, dissolving the washed precipitate in ammonia, and adding to an ammoniacal cadmium solution, whereby cadmium sulphide is precipitated. It is collected, washed, and transferred to a beaker half full of water. The sulphide is then rapidly titrated with iodine after the addition of 75 c.c. of approximately 10% hydrochloric acid, using starch as indicator. Care must be taken that hydrogen sulphide is not lost during the titration. The results quoted indicate that the method is quite trustworthy for the accurate estimation of quantities of arsenic as small as 0·03—0·05%. G. F. M.

Estimation of Small Quantities of Boric Acid. G. Halphen (*Ann. Falsif.*, 1915, **8**, 1—2).—The following modification of Bertrand and Agulhon's method (A., 1914, ii, 146) is recommended as being more trustworthy than the process described originally. The distillate containing the methyl borate is collected in a vessel containing 0·2 c.c. of $N/1$-sodium hydroxide solution, the solution is then evaporated to dryness in a small test-tube, and the residue dissolved in 1 c.c. of water and 2 c.c. of hydrochloric acid (D 1·165). One c.c. of a solution of turmeric in ethyl acetate is now added, and, after fifty minutes, the red coloration obtained is compared with those of standard boric acid solutions prepared under similar conditions. The turmeric solution employed should be of such strength that its colour is equal to that of a 0·16% potassium chromate solution. W. P. S.

Estimation of Carbon Monoxide by the Iodine Pentoxide Method. Victor Froboese (*Zeitsch. anal. Chem.*, 1915, **54**, 1—11).—In this method, which depends on the oxidation of the carbon monoxide according to the equation $I_2O_5+5CO=5CO_2+I_2$, the iodine pentoxide should be heated at 100° during the reaction. Hydrogen is also oxidised by iodine pentoxide, iodine being liberated; at 70° the reaction with hydrogen is but slight, but at 160° large quantities of free iodine are formed. The quantity of carbon monoxide present may be ascertained by estimating the carbon dioxide formed or the iodine liberated. Estimation of the carbon dioxide yields the more trustworthy results; the carbon dioxide is collected in an excess of barium hydroxide solution, and, at the end of the experiment, this excess is titrated, or the barium carbonate may be separated, converted into barium sulphate, and weighed as such. The gas in which the carbon monoxide is to be estimated must be freed from carbon dioxide, acetylene, and ethylene. Small quantities of carbon monoxide in air may be estimated approximately by titrating the liberated iodine provided that air free from carbon monoxide and dioxide is passed over the heated iodine pentoxide for one hour before and after the passage of the air under examination. The quantity of carbon monoxide in a gas does not affect the method if the rate of flow of the gas through the apparatus does not exceed 1 litre per hour.

W. P. S.

Microscopic Tests on Opaque Minerals. Everend L. Bruce (*Chem. News*, 1915, **111**, 121—122).—An attempt to draw up a scheme, based to some extent on previously published work, for the microscopic determination of opaque minerals when occurring in small grains in rocks or ores. The specimen is first highly polished, and is then examined for colour and appearance, using obliquely incident light. Etching is tried first with concentrated hydrochloric, then with nitric, and finally if still unattacked with a mixture of both acids. To distinguish minerals behaving in the same manner under etching, micro-chemical and physical tests are adopted, as, for example, acid ferrocyanide solution for iron, dimethylglyoxime for nickel, nitric acid and ferrocyanide for copper, nitric acid followed by hydrochloric acid for silver, and by water in addition for bismuth. The scheme depends for its main division on the colour of the polished mineral, and in each colour division, subdivisions are made by the etching test. A tabular summary of the scheme is appended. G. F. M.

Volumetric Estimation of Metals by means of Arsenic Acid. J. Valentin (*Zeitsch. anal. Chem.*, 1915, **54**, 76—89).—The process consists in treating the metallic salt solution with an excess of monopotassium arsenate solution, diluting the mixture to a definite volume, and, after twenty-four hours, separating the insoluble arsenate by filtration, and estimating the excess of arsenate in an aliquot portion of the filtrate by adding hydrochloric acid and potassium iodide, and titrating the liberated

iodine with thiosulphate solution. In the case of magnesium, calcium, strontium, barium, lead, and manganese, the precipitation with the arsenate solution is carried out in an ammoniacal solution; bismuth is precipitated in neutral solution, zinc and cadmium in the presence of sodium hydrogen carbonate, and the mixture then rendered neutral with acetic acid, nickel, and cobalt in the presence of sodium acetate, and aluminium and chromium in very dilute acetic acid solution. W. P. S.

Comparison of the Reactions of Sodium Hydrogen Carbonate and Natural Vichy Salts with Phenolphthalein. A. MALLAT (*J. Pharm. Chim.*, 1915, [vii], **11**, 113—117).—Vichy salts and Vichy mineral waters behave towards phenolphthalein in exactly the same way as do sodium hydrogen carbonate and solutions of the same in water containing carbon dioxide, respectively. The dissociation of the Vichy salts may appear in some cases to be slightly more rapid when heated than that of sodium hydrogen carbonate, but this is due to the presence in the salts of carbonates other than sodium hydrogen carbonate. W. P. S.

Estimation of Zinc as Zinc Ammonium Phosphate, and its Application to the Separation of Zinc (from other Metals). P. ARTMANN (*Zeitsch. anal. Chem.*, 1915, **54**, 89—102).—The neutral zinc solution is heated to 70° and treated with an excess of diammonium phosphate solution, 2 grams of ammonium chloride being also added for each 0·1 gram of zinc present. The mixture is maintained at 70° for fifteen minutes, cooled, the precipitate collected, washed, and titrated iodometrically (A., 1910, ii, 241); three atoms of iodine correspond with one atom of zinc. One hundred c.c. of water at 17·5° dissolve 0·00145 gram of zinc ammonium phosphate, corresponding with 0·00053 gram of zinc, and the results are corrected for this amount, the volume of the reacting solution and the wash-water being taken into account. Zinc may be separated from copper by precipitation as zinc ammonium phosphate provided that ammonium tartrate is present in the solution; when the proportion of copper is large, a double precipitation is necessary. W. P. S.

Precipitation of Zinc and Manganese by Ammonium Sulphide. E. SEELIGMANN (*Zeitsch. anal. Chem.*, 1915, **54**, 104).—Ammonium salts do not interfere with the precipitation of zinc by ammonium sulphide, but affect the precipitation of manganese; in the latter case, a small quantity of hydrogen peroxide should be added to the manganese solution before an excess of ammonia is introduced. W. P. S.

Test for Nickel in Hardened Oils. FR. PRALL (*Zeitsch. angew. Chem.*, 1915, **28**, 40).—The best method for testing for nickel in hardened oils is as follows. One hundred to two hundred grams of the oil are ashed in a platinum dish. The ash is dissolved in dilute hydrochloric acid, the solution heated to drive off the greater part

of the acid, and then saturated with ammonia. After keeping for some hours, the precipitated iron and aluminium hydroxides are collected, the filtrate evaporated to dryness, and the residue treated with ammonia and alcoholic dimethylglyoxime solution. 0·01—0·1 Mg. of nickel in 100 grams of oil gives a red coloration.

T. S. P.

The Electrolytic Deposition of Nickel from Chloride Solutions. R. Riedel (*Zeitsch. Elektrochem.*, 1915, **21**, 5—19).—In the extraction of copper from sulphides containing nickel, large quantities of nickel chloride solutions are obtained, from which the nickel is removed electrolytically. The author has investigated the conditions of electrolysis at the ordinary temperature in the presence of free hydrochloric acid and in the presence of acetic acid. The current efficiency and the conditions under which a good coherent metallic deposit are obtained in the two cases are compared. The current efficiency over the range 100—80% has been quantitatively determined in its relation to the concentration of hydrochloric acid and acetic acid. In the case of hydrochloric acid, carbon anodes were used, and in the case of acetic acid, both carbon and nickel anodes were used. The current efficiency decreases with an increase in the acid concentration. With hydrochloric acid it is 80% when the acid concentration has reached 0·07%, whilst in the case of acetic acid this value is only reached with 1·0% of acid. In consequence of this high concentration of acetic acid, its use would remove the necessity of a very troublesome controlling of the acid concentration during the electrolysis, which is always necessary when hydrochloric acid is used. Since, in order that the nickel should be deposited in a usable form, it is necessary that a definite concentration of hydrogen ions should be maintained, which when an operation is left to itself speedily ceases to be the case, on account of the rapid removal of the small quantity of acid allowable, whilst the larger amount of slightly dissociated acetic acid automatically keeps the hydrogen ion concentration at the right point. The current efficiency increases with the concentration of nickel in the solution. Using a current density of 190 amperes per square metre with a solution containing 4—10% nickel, the efficiency fluctuates between 80% and 90%, and with a current density of 350 amperes per square metre it varies between 85% and 95% in a 1% acetic acid solution. To obtain a continuous coherent deposition of nickel, it is shown that the current density must be kept within limits which are special for each solution, and depend on the concentration of the solution in nickel and free acid, on the nature of the free acid, the purity of the solution, and the method of stirring the liquid. A continuous stirring of the electrolysis bath is only necessary in the case where the solution becomes alkaline. It is shown that porous deposits can be avoided by using a current density which just produces the coherent deposit; a higher value may be used only with a higher concentration of nickel or of acid. The presence of many metallic ions in a hydrochloric acid solution of nickel chloride is

unfavourable to the formation of a coherent deposit. The order in increasing harmfulness is $Cu^{\cdot}$, $Cu^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $Zn^{\cdot\cdot}$, and $Pb^{\cdot\cdot}$. In an acetic acid solution experiments were made only with zinc and lead as impurity, since it was shown that the deposit of nickel is not so sensitive to the presence of impurities as in the case of hydrochloric acid solutions. The minute traces of foreign metals suffice in a hydrochloric acid solution to produce a spongy nickel effect, whilst in acetic acid solutions very considerable quantities of impurities may be added before any influence is shown in the nature of the deposit. If a spongy deposit is once produced, no change of the conditions of electrolysis is sufficient to bring it back to the coherent condition. As a general result of the work, it follows that in the electrolysis of nickel chloride solutions the addition of hydrochloric acid is harmful, and cannot be considered in the technical electrolysis; a weakly dissociated acid is required, and this is found in acetic acid. J. F. S.

A Rapid Method for the Estimation of Chromium in Iron and Steel. Heinrich Tusker (*Chem. Zeit.*, 1915, **39**, 122).—Two grams of iron shavings are dissolved in 50 c.c. of 20% sulphuric acid, and, after dilution with water to 300 c.c., 8 grams of ammonium persulphate are added. The liquid is boiled until permanganic acid or hydrated manganese dioxide commences to precipitate. In the latter case, which occurs when more than about 0·3% of manganese is present, the boiling is continued for ten minutes in order to decompose the excess of persulphate and to concentrate the solution somewhat. In either case, 5 c.c. of hydrochloric acid are next added, and the solution boiled for five minutes until the manganese has been reduced and the smell of chlorine is no longer apparent. The chromic acid is not reduced by the hydrochloric acid, and, after diluting to about 500 c.c., may be titrated by means of ferrous sulphate and permanganate in the usual way. The results quoted show excellent agreement among themselves and with those obtained by more complex methods. G. F. M.

Estimation of Organic Matter in Potable Water. J. D. Filippo and H. J. Backer (*Chem. Weekblad*, 1915, **12**, 150—156. Compare this vol., ii, 109).—A continuation of the authors' research on the estimation of organic matter in water analysis. The permanganate value is unaffected by the presence of either ferric salts or nitrates, or by that of appreciable quantities of ammonium salts in acid solution. In alkaline solution, ammonium salts exert a slight influence. For water containing a moderate proportion of organic matter and more than 500 mg. of chlorine per litre, the oxidation should be carried out in alkaline solution. If the proportion of organic material is very small, this limit should be reduced to 250 mg. No correction is necessary with a sulphur content of 0·05 mg. per litre. In presence of nitrites, each mg. of NO_2 per litre necessitates the subtraction of 1·374

from the permanganate value, but no correction is necessary if the NO_2 does not exceed 0·1 mg. per litre.

In presence of ferrous salts and only a trace of nitrite, the oxidation should be carried out in acid solution, and corrected by deducting the amount of permanganate reduced in the cold by the acidified water. When the nitrite content is high, the ferrous salts should be oxidised by agitation with air, and the nitrite corrected for by the method indicated in the preceding paragraph.

Equally accurate results are obtained by the alkaline and acid oxidation, the oxalic acid titration, and the iodometric method. When proteins are present, the acid method is the best.

A. J. W.

Estimation of Gasolene Vapour in Air. G. A. Burrell and I. W. Robertson (*J. Ind. Eng. Chem.*, 1915, **7**, 112—113).—Two methods were used in the experiments described. In the first, the mixture of gasolene vapour and air was introduced into a glass vessel at ordinary pressure, cooled by means of liquid air, and the air then withdrawn by a pump; after closing the vessel, the liquid air was removed, the gasolene vaporised, and the pressure of the vapour measured. The other method consisted in burning the gasolene vapour with air or oxygen, and calculating the percentage quantity present from the amount of carbon dioxide obtained or from the resulting decrease in volume. Although gasolene vapour consists of a mixture of paraffins, the results obtained in the combustion method, by calculating the data on a pentane basis, agreed with those found by separating the gasolene vapour with liquid air. When pentane is burnt in oxygen, the contraction is 4 vols. and the carbon dioxide measures 5 vols.; therefore the volume of the carbon dioxide divided by 5, or the contraction divided by 4, gives the volume of gasolene vapour in the air.

W. P. S.

Estimation of the Percentage of Toluene in Commercial Toluol. H. G. Colman (*J. Soc. Chem. Ind.*, 1915, **34**, 168—170; from *J. Gas Lighting*, 1915, **129**, 196—198).—The sample is distilled from a standard Engler flask under the prescribed conditions, and the volumes of the fractions collected below 105°, from 105—117°, and above 117°, are noted. By the aid of a table, which is based on a large number of distillations of mixtures of benzene, toluene, and xylene, the percentage of toluene may be derived from the volumes of the extreme fractions. The table is only applicable to mixtures which contain 50—75% of toluene. Other samples must be diluted with benzene, toluene, or xylene so that the extreme fractions are, each of them, not less than 5% nor more than 50% of the total distillate.

If the sample contains paraffins, 100 c.c. may be fractionated with a Young twelve-bulb column, and the percentage of the toluene fraction, 107—115°, corrected by measuring its density. For every 0·001 that the density is below 0·868, a reduction of 0·75% is made.

J. C. W.

Estimation of Toluene in Commercial Solvent Naphtha. H. G. COLMAN (*J. Soc. Chem. Ind.*, 1915, **34**, 217; from *J. Gas Lighting*, 1915, **129**, 314—315).—Sufficient of the sample is distilled at the rate of one drop per second, with an efficient fractionating column, to give at least 35 c.c. of distillate below 138°. If 200 c.c. of the sample fail to yield 35 c.c. of this fraction, it may be considered to be practically free from toluene. Otherwise, 35 c.c. of the distillate are mixed with 50 c.c. of toluene and 15 c.c. of benzene, and examined as above (preceding abstract). J. C. W.

The Rate of Saponification of Linalyl, Terpenyl, and Geranyl Acetates. C. L. BARILLET and R. BERTHELÉ (*Bull. Soc. Chim.*, 1915, [iv], **17**, 20—28. Compare Schimmel & Co., A., 1910, i, 327, 756; 1911, i, 893).—A study of the rates of saponification of the three esters linalyl, terpenyl, and geranyl acetates, either alone or in mixtures of two or three together, the temperature of saponification and amount and concentration of the alcoholic potassium hydroxide employed being varied. The results, whilst not giving the necessary data for accurate determination of the amounts of the respective esters present in a mixture, show that, using 1·5 grams of the ester and 25 c.c. of $N/2$-alcoholic potassium hydroxide, and performing two saponifications, one at 15—16° for twenty-four hours, and the other at the boiling point for three hours, it is possible to get an indication of the adulteration of oil of bergamot by the addition of terpenyl acetate. A difference of 1% between the saponification numbers obtained under the above conditions is an indication of adulteration. W. G.

Microscopical Detection of Potato Starch in Bread. G. SCHÜTZ and L. WEIN (*Chem. Zeit.*, 1915, **39**, 143).—Potato starch takes up certain coal-tar colours much more rapidly than starches derived from wheat and rye, and its presence may therefore be readily detected microscopically in a suitably stained preparation. The procedure is as follows. A few breadcrumbs are disintegrated by moistening with water and gently pressing with a cover slip. The preparation is then dried by rapidly passing the slide through the flame, and a drop of an aqueous solution of neutral-red, methylene-blue, or, best of all, thionin, is applied for a definite time, varying from one and a-half to three minutes, according to the dye. Excess is then washed away, and the stained specimen examined under a low power. With neutral-red, wheat and rye starch grains appear colourless, and potato starch rose-red, and a similar differentiation exists with methylene-blue. With thionin, the wheat and rye starch, as before, is colourless, potato starch lilac, the parenchyma of the potato deep violet, and the tissues of the seed coat of the wheat and rye, and the cork and other thickened cells of the potato skin (if present), blue. If the bread has been baked from boiled potatoes instead of potato meal, starch grains are generally disrupted, and a more careful preparation of the specimen is necessary, avoiding heat and pressure in order

not to destroy the outlines of the so-called paste cells, which are then differentiated with thionin by a red coloration if of potato origin. By making comparative preparations, the quantity of potato meal added to the bread can be roughly estimated.

G. F. M.

Recent Progress in the Analysis of Cellulose and Cellulose Derivatives. J. F. Briggs (*Analyst*, 1915, **40**, 107—120).—In giving a synopsis of the progress in the chemistry of cellulose and its derivatives, the author discusses the subject under the headings: Estimation of cellulose in raw materials, nature of lignocellulose, modified cellulose, specification of "normal cotton" for nitrating, estimation of moisture, cellulose and alcohol, and analysis of cellulose esters. For the estimation of cellulose in raw materials, the chlorination method appears to be the most trustworthy (compare A., 1913, ii, 736; 1914, i, 148). The theory of Wislicenus and Kleinstück, that lignocellulose is an adsorption compound of interpenetrating colloids, appears to be generally acceptable, and receives support by the recent isolation of lignin as a definite residue (A., 1913, i, 955). For all practical purposes, "dry" cellulose may be obtained without appreciable loss of weight by decomposition by heating in dry air at 105° to constant weight; cellulose may also be dried completely in twenty hours by exposing it over phosphoric oxide at 35° and under reduced pressure. Attention is drawn to the fact that when cellulose which has been washed with water is washed subsequently with alcohol, the alcohol cannot be completely expelled by heating. Since cellulose itself is sensitive to the agents employed for the decomposition of its esters, the latter are best saponified by treatment for forty-eight hours with a cold mixture of equal volumes of N/1-sodium hydroxide solution and 95% alcohol. Stein's method (A., 1913, i, 1305) may be employed for the hydrolysis of esters of modified cellulose. Ambronn has described a polariscopic method (A., 1913, ii, 897) for the examination of nitrocellulose, and von Hottenroth a process for the estimation of sulphuric acid in cellulose compounds (A., 1914, ii, 501).

W. P. S.

Estimation of Crude Fibre. R. Fanto and W. Nikolitsch (*Zeitsch. anal. Chem.*, 1915, **54**, 73—76).—The filtration of the acid and alkaline solutions in the estimation of crude fibre may be rendered more rapid by the use of a filter-thimble of such capacity that it will hold the whole of the solution. The acid or alkaline digestion mixture is poured into the thimble, and when the liquid portion has passed through, the thimble is suspended in water; the latter passes inwards through the walls of the thimble, which is then raised, and the washing of its contents is continued in this way. The procedure prevents the fine particles of substance from clogging the walls of the thimble. When washed, the crude fibre is rinsed into a platinum basin, dried, and weighed. W. P. S.

Estimation of Formic and Acetic Acids, and the Separation of these Acids in Very Dilute Solutions. EMIL HEUSER (*Chem. Zeit.*, 1915, **39**, 57—59).—Wenzel's method for the determination of acetyl groups in organic compounds (A., 1898, i, 234) is applied with some modifications to the estimation of formic and acetic acids in dilute solution. To carry out the process, a large excess of phosphoric acid is added to the solution, and the distillation is performed rapidly under diminished pressure at a temperature of about 50°. Instead of distilling in an atmosphere of hydrogen, air, freed from carbon dioxide by passing through a wash flask containing sodium hydroxide solution, is bubbled through the liquid in the distilling flask by means of a capillary. Between this flask and the condenser a second flask is placed, filled with glass beads and immersed in a boiling water-bath, in order to prevent phosphoric acid being blown over into the distillate. When the solution has been reduced to about 50 c.c., it is again diluted with water, and the distillation continued until the volume has been once more reduced to 50 c.c. The whole distillation requires from one and a-half to two hours, and total volatile acids will in that time have been expelled, and may be titrated in the distillate. The separate determination of a mixture of formic and acetic acids depends on the oxidation of the former with dichromate and sulphuric acid in a solution of the free acids, prepared as above described, and the subsequent distillation of the acetic acid. Carried out in the manner hitherto employed, that is, by steam distillation, or direct distillation of the acid liquid with or without the addition of a phosphate, the results are highly unsatisfactory, but if this second distillation is performed in vacuum in the same manner as the first, using air free from carbon dioxide and a safety flask to prevent sulphuric acid blowing over, perfectly accurate results are obtained. G. F. M.

The Estimation of Lactic Acid in the Extracts of Organs as Carbon Monoxide. RICHARD MEISSNER (*Biochem. Zeitsch.*, 1915, **68**, 175—190).—The estimation depends on the reaction, $C_3H_6O_3 = C_2H_4O + H_2O + CO$, which takes place when lactic acid or a lactate is treated with concentrated sulphuric acid. The gas is collected in a nitrometer filled with 50% potassium hydroxide solution, and the reaction is carried out in a current of carbon dioxide. The methods of separating the lactic acid from the organs are the same as those employed in other processes, as, for example, in the method of von Fürth and Embden. S. B. S.

Estimation of Oxalic Acid in Vegetable Products. A. GRÉGOIRE and E. CARPIAUX (*Bied. Zentr.*, 1915, **44**, 20—22; from *Annuaire Stat. Agron. Gembloux*, 1913, **2**, 140).—The ground substance (5 grams) is heated on a water-bath with 20 c.c. of 4% hydrochloric acid for an hour, treated with a little dry sodium sulphate, and, when cold, with about 100 c.c. of 94% alcohol. It is then filtered, washed with alcohol, and the filtrate treated with a slight excess of ammonia. After evaporating off the alcohol, it is treated with

water containing hydrochloric acid, and filtered. The oxalic acid is then precipitated with calcium acetate in presence of a little acetic acid, filtered, washed, and redissolved in hydrochloric acid. It is then evaporated to dryness, treated with 25% sulphuric acid and enough anhydrous sodium sulphate to produce a dry mass. This is extracted five or six times with ether, the extract, with a little ammonia, evaporated to dryness, the residue dissolved in water, and again precipitated with calcium acetate in presence of acetic acid. N. H. J. M.

Estimation of Small Quantities of Hydrocyanic Acid. ARNO VIEHOEVER and CARL O. JOHNS (*J. Amer. Chem. Soc.*, 1915, **37**, 601—607).—Experiments are described which have led to the following method for estimating small quantities of hydrocyanic acid, such as are obtained from cyanogenetic plants. The distillate containing the hydrocyanic acid is rendered slightly alkaline with sodium hydroxide, and is then concentrated by distillation under reduced pressure until less than 1 c.c. of liquid remains in the distilling flask. From 0·2 to 0·5 c.c. of freshly prepared 3% ferrous sulphate solution, and about 0·05 gram of potassium fluoride, are added. The flask is now exhausted by means of a water vacuum pump, and after five to ten minutes it is detached from the pump, and the mixture is acidified with 30% nitric acid. The blue colour appears at once unless only traces of hydrocyanic acid are present; in the latter case, the mixture may need to be warmed to 50° before the colour appears. The product is then diluted to a volume which would give a depth of colour suitable for comparison with a suspension of Prussian-blue, made from 1 mg. of potassium cyanide diluted to 25 c.c. The comparison may be made with the Duboscq colorimeter. The method has been found to be very accurate.

This method also affords a very delicate test for the presence of cyanides; 0·00002 gram of potassium cyanide can be detected with certainty. The test can also be applied microchemically to sections of cyanogenetic plants. E. G.

Estimation of Benzoic Acid in Urine. G. W. RAIZISS and H. DUBIN (*J. Biol. Chem.*, 1915, **20**, 125—128).—The method proposed is a modification of that of Folin and Flanders (A., 1911, ii, 1039). A solvent was sought which does not produce emulsions with urine; toluene is the best, and is superior to chloroform (used by Folin and Flanders); it is an excellent solvent for benzoic acid, and practically does not dissolve hippuric acid.

W. D. H.

Colour Reaction of Gallic Acid and Tannin (Tannic Acid) and its Application. CARL TH. MÖRNER (*Pharm. Zentr.-h.*, 1915, **56**, 13. Compare A., 1913, ii, 737).—The reaction described by Schewket (*loc. cit.*) has been mentioned previously (Griessmayer, *Zeitsch. anal. Chem.*, 1872, **11**, 43). The author also noticed, in the year 1890, that a gum-wash, consisting of a dilute alcoholic

solution of iodine, potassium iodide, tannin, and camphor, yielded a violet coloration when diluted with a large volume of water.
W. P. S.

Determination of the Freezing Point of Milk. N. SCHOORL (*Chem. Weekblad*, 1915, **12**, 220—222. Compare this vol., ii, 112).—A criticism of the experimental method previously described for determining the freezing point of milk. A. J. W.

Standardisation of a Freezing-point Thermometer. N. SCHOORL (*Chem. Weekblad*, 1915, **12**, 222—225).—Thermometers for determining the freezing point of milk can be standardised by means of a 12·2% aqueous solution of potassium nitrate, with the eutectic $-2·86°$, and a 4·5% aqueous solution of barium nitrate, with the eutectic $-0·71°$. A. J. W.

The Freezing Point of some Abnormal Milks. J. B. HENDERSON and L. A. MESTON (*Chem. News*, 1915, **111**, 51—53).—Analyses made in the Government Laboratory, Brisbane, of milk from two herds of cows, which had been grazing in a neighbourhood where the grass was poor both in quality and quantity, showed that whilst fat, solids not fat, and nitrogen were all low, and chlorine was abnormally high, yet the freezing point was in every case practically normal. There was no question of adulteration with water, which, judging only by the solids not fat standard, an analyst might have assumed. No dairyman could, moreover, have so accurately adjusted the addition of common salt as exactly to compensate for the raising of the freezing point by the addition of water. Stress should therefore be laid on the fact that the freezing point, or osmotic pressure, is the only constant factor of a pure milk, since the mammary glands of the cow, when unable to obtain the correct proportion of milk sugar and other foodstuffs, adjust the osmotic pressure by adding an extra proportion of common salt from the blood. A variation of as much as 0·01° from the normal, $-0·55°$, is very rare, even in milks of widely varying fat and solids not fat content. The freezing point is, of course, only a criterion of the purity, not of the quality, of a milk sample, as the above instance shows. G. F. M.

Solidifying Point of Mutton Tallow. ROBERT MELDRUM (*Chem. News*, 1915, **111**, 98—99).—The erratic solidification of tallow (A., 1914, ii, 225) is, to some extent, accounted for by the influence of the liquid glycerides which it contains, but even after most of the olein has been removed by extraction with ether, the solid glycerides still exhibit variations of 2·5° in the "zero" point, that is, the point to which they must be supercooled before solidification commences, and 1·8° in the rise of temperature after solidification has commenced. The solidifying point is 3·5° lower than the melting point, but all these discrepancies are nearly 100% less than with the original tallow. Based on numerous experiments, the author considers the true explanation is that fluctua-

tions in the melting point are due to errors in manipulation and observation, and in the solidifying point to speed of crystallisation. The glycerides appear to require supercooling to start rapid crystallisation, and the problem which presents itself in the solidification is the failure to attain their normal solidifying point when crystallisation sets in. This would apparently point to the fact that the melting had lowered the solidifying point through some molecular change, according to Chittenden's theory; but the true explanation is probably the purely thermal one, that the latent heat of fusion is insufficient to raise the supercooled liquid to the normal solidifying point, the more so when mixtures of solids and liquids are dealt with. G. F. M.

Distinction Between Fats of Animal and Vegetable Origin. F. H. VAN LEENT (*Chem. Weekblad.*, 1915, **12**, 86—92).—The presence of vegetable fat in animal fat up to 10% can be detected by the aid of the fact that the melting point of the cholesteryl acetates formed is always higher than that of the pure cholesteryl acetate derived from the animal fat itself. The method is not applicable to the detection of animal fats in vegetable fats. A. J. W.

Formaldehyde Reactions. E. SALKOWSKI (*Biochem. Zeitsch.*, 1915, **68**, 337—346).—The reaction of Leach is very sensitive, but it fails in the presence of relatively large amounts of acetaldehyde. ω-Hydroxymethylfurfuraldehyde also gives a positive result with Leach's reagents. This substance also gives a coloration in the reactions of Rimini and of Schryver, but the shade of colour produced is not exactly that formed by formaldehyde, and is not obtained in dilute solutions, so that the two substances are not likely to be mistaken for one another. Bono's reaction for formaldehyde cannot be used in the presence of ω-hydroxymethylfurfuraldehyde. Least influenced by this substance is Rimini's reaction, both in its original form and when hydrogen peroxide is used instead of ferric chloride; it is less sensitive, however, than Schryver's reaction. As ω-hydroxymethylfurfuraldehyde is always formed by the action of acids on carbohydrates, it must always be sought for in certain cases when the existence of formaldehyde is investigated. S. B. S.

Estimation of Formaldehyde and Methyl Alcohol in Aqueous Solutions (Analysis of Formalin). G. LOCKEMANN and F. CRONER (*Zeitsch. anal. Chem.*, 1915, **54**, 11—26).—In solutions containing formaldehyde and methyl alcohol, the former may be estimated by titrating the free acid or alkali formed when the solution is treated with hydroxylamine hydrochloride or sodium sulphite, respectively, the equations showing the reactions being $CH_2O + NH_2{\cdot}OH,HCl = CH_2{:}N{\cdot}OH + H_2O + HCl$ and

$$CH_2O + Na_2SO_3 + H_2O = OH{\cdot}CH_2{\cdot}SO_3Na + NaOH.$$

Methyl alcohol and formaldehyde are then estimated together by oxidation with potassium permanganate, as described by Hetper (A., 1913, ii, 158). W. P. S.

Detection of Vanillin in Quinine Wines. A. C. CHAUVIN (*Ann. Falsif.*, 1914, **7**, 420—422).—A test proposed by Lecomte depends on the reddish-coloured zone which is obtained when an alcoholic phloroglucinol solution is poured on the surface of an ethereal extract of the wine acidified with hydrochloric acid, but the author points out that furfuraldehyde and its derivatives also give this reaction. As the latter substances are frequently present in this class of wine, a positive reaction does not definitely indicate the presence of vanillin. W. P. S.

Reactions of Vanillin. E. P. HÄUSSLER (*Zeitsch. anal. Chem.*, 1915, **54**, 104. Compare A., 1914, ii, 592).—When pepsin is mixed with dilute alcohol and a small quantity of vanillin, and the mixture evaporated, a yellow coloration is obtained; this changes to brownish-violet and then to brownish-red on the addition of 10% hydrochloric acid. Concentrated hydrochloric acid changes the yellow colour to violet, and the mixture becomes black on evaporation. The pepsin employed yielded a brown coloration, but no trace of violet, when treated with hydrochloric acid in the absence of vanillin; it also gave a slight biuret reaction. The author has not ascertained whether the reaction with vanillin was due to the pepsin itself or to the presence of proteins in the same. W. P. S.

The Action of Chlorinated Solvents on the Hard Copals. CH. COFFIGNIER (*Bull. Soc. Chim.*, 1914, [iv], **15**, 780—783).—The author has determined the behaviour of Zanzibar, Madagascar, and Demerara copals in the presence of the following solvents: dichloroethylene, trichloroethylene, tetrachloroethylene, tetrachloroethane, and pentachloroethane. The amount of material insoluble in the boiling solvent is given in each case. The use of tetrachloroethane enables Madagascar copal to be distinguished from those of Zanzibar and Demerara, the former being the only one to give a solution which approaches completion. W. G.

New Reaction of Cocaine. F. PISANI (*Pharm. J.*, 1914, **93**, 589; from *Rend. Soc. Chim. Ital.*, 1914, **6**, 132).—When cocaine or its hydrochloride is heated with a few drops of concentrated sulphuric acid containing 2% of formaldehyde, a wine-red coloration is produced. The coloration increases in intensity as the temperature rises, but soon disappears, leaving a brownish-grey precipitate. The reaction may be obtained with 1 mg. of cocaine, but is not given by atropine, quinine, cinchonine, brucine, strychnine, morphine, *apo*morphine, codeine, and narcotine. Papaverine, however, also gives a wine-red coloration, but this changes to yellow, reddish-brown, and orange. W. P. S.

Influence of the Presence of Acetoacetic Acid in Urine on the Colorimetric Estimation of Creatinine and Creatine. L. BINET, DEFFINS, and RATHERY (*J. Pharm. Chim.*, 1915, [vii], **11**, 41—42; from *Compt. rend. Soc. Biol.*, 1914, **49**).—The presence of

3·90 grams of acetoacetic acid per litre of urine may cause an error of 40% in the separate estimations of the creatinine and creatine, but the total quantity of creatine is not affected. This error may be avoided by adopting a method proposed by Graham and Poulton (A., 1914, i, 228). Ten c.c. of the urine are mixed with 1 c.c. of 10% phosphoric acid and heated at 65—70° for forty-five minutes under a pressure of 210 mm.; the mixture is then cooled and neutralised with 10% sodium hydroxide solution. In some cases it is necessary to continue the heating for one hour or more. W. P. S.

Sensitive Reaction of *apo*-Morphine. L. Grimbert and A. Leclère (*J. Pharm. Chim.*, 1915, [vii], **11**, 23—24).—Five c.c. of *apo*-morphine hydrochloride solution are boiled for a few seconds with 5 drops of saturated mercuric chloride solution and 5 drops of 10% sodium acetate solution, then cooled, and shaken with 2 c.c. of amyl alcohol; the latter is coloured blue if the solution under examination contains even as little as 1 part of *apo*morphine hydrochloride per 500,000 parts. When more *apo*morphine is present, a blue precipitate is formed on boiling the mixture; this precipitate is soluble in amyl alcohol. W. P. S.

Detection and Estimation of "Saccharin" in Complex Mixtures. S. Condelli (*Ann. Chim. anal.*, 1915, **20**, 40—41; from *Staz. sperim. agrar. ital.*, 1914, 308).—In the case of solid substances, from 10 to 50 grams are heated at 40° for thirty minutes with a saturated solution of magnesium sulphate and magnesium oxide, then diluted with the same solution to a definite volume, and filtered. A small quantity of sodium tannate and alcohol may be added, if required, to cause the precipitate to separate rapidly. An aliquot portion of the filtrate is acidified with sulphuric acid, extracted with a mixture of ether and light petroleum, and the ethereal solution evaporated; the residue is dissolved in sulphuric acid, treated with potassium permanganate, then extracted with ether, and the residue obtained on evaporating the ether is dried and weighed. The usual tests for identifying "saccharin" are then applied. When the substance under examination is a liquid, it is saturated with magnesium sulphate, magnesium oxide is added in quantity sufficient to render the mixture alkaline, and the separation then carried out as described. If the substance contains fat, the alkaline solution is extracted with light petroleum before being rendered acid, and extracted with the mixture of ether and light petroleum.
W. P. S.

Detection and Estimation of Bacterial Indole. Frederick C. Lewis (*J. Path. Bact.*, 1915, **19**, 429—442).—The Ehrlich test gives variable results. A new method is devised, of which the main feature is preliminary extraction with chloroform.
W. D. H.

General and Physical Chemistry.

Burners Fed with Saline Spray for Polariscopic and Spectroscopic Use. Ernst Beckmann and Hans Lindner (*Ber.*, 1914, **47**, 2722—2728).—Burners especially adapted to the production of flame colorations have been described, in which the required metal is fed into the flame as spray produced by electrolysis of a solution (Beckmann, A., 1912, ii, 1049; Riesenfeld and Wohlers, A., 1906, ii, 593), or by chemical generation of a gas in the solution (Beckmann, A., 1907, ii, 209; Riesenfeld, A., 1913, ii, 997). The same idea has been extended to the production of arc spectra (Riesenfeld and Pfützer, A., 1913, ii, 1074).

In the present investigation a similar principle has been applied to the oxy-hydrogen flame in which the hydrogen burns in an atmosphere of oxygen, the salt spray being fed into the latter. The porcelain tube of the burner has to be protected by a nickel fitting. On account of the high temperature the spectra are richer in lines than when produced under the ordinary conditions, but with sodium light this modification in the colour is insufficient to affect its value for polarimetric work, and the light can be purified, if desired, by passage through a suitable light-filter, such as a solution of potassium dichromate. The spectra produced are comparable in intensity with the corresponding arc spectra.

It is shown by the result of experiments that for sensitiveness the electrolytic method for producing the spray has no advantage over that in which the spray is produced by the action of coppered zinc on an acid. D. F. T.

The Spectra of Carbon Monoxide and Carbon Dioxide. Karl Hof (*Zeitsch. wiss. Photochem.*, 1914, **14**, 39—55, 69—88).—Experiments have been made to ascertain the influence of the nature of the electrical discharge on the spectra of carbon monoxide and carbon dioxide, in particular the influence of capacity, self-induction, current density, electrode potential, and gas pressure.

It is probable that the various known spectra are exhibited under all conditions of electrical discharge, and that changes in the character of the discharge produce changes in the relative intensities of these spectra which correspond more or less closely with changes in the dissociation equilibria.

In the visible portion of the spectrum, the influence of capacity is to increase the intensity of the Swan and the line spectrum, and to diminish that of the carbon monoxide bands. Self-induction increases the length of the Swan and cyanogen bands. Under the same conditions of experiment the carbon line spectrum varies according to whether it is produced by discharge through the monoxide or the dioxide.

In the ultra-violet region the effect of capacity is to broaden the bands and reduce their intensity. Self-induction has the opposite effect.

From experiments in which the gases were made to flow through the discharge tube at different rates, it is probable that the second negative group of bands must be attributed to the carbon dioxide molecule. The influence of gas pressure on the nature of the spectra suggests that the line spectrum, the Swan spectrum, and the fourth positive group must be attributed to the products of dissociation.

The same spectra, with essentially the same distribution of intensities, are obtained by continuous and alternating discharge.

The bands described by Deslandres and D'Azambuja (*Compt. rend.*, 1905, **140**, 917) could not be identified with any certainty.

H. M. D.

The Red Argon Spectrum. EMIL PAULSON (*Physikal. Zeitsch.*, 1914, **15**, 831—833).—An investigation of the red argon spectrum has been carried out with the object of ascertaining whether the quadruplet found by Rydberg was represented in the long wave-length portion of the spectrum. It is shown from the results that the lines now measured can be brought into the Rydberg arrangement. In the cases of the difference 847·71 and those of 802·91 and 606·80 the agreement is not so good, the former being too high and the latter too low.

J. F. S.

The Continuous Background in the Bunsen Flame Spectra of the Alkali Metals. HEINRICH THEISSEN (*Zeitsch. wiss. Photochem.*, 1914, **14**, 125—136, 148—170).—In addition to the characteristic lines, the Bunsen flame spectra of the alkali metals exhibit a more or less intense so-called continuous background, the investigation of which was the chief object of the experiments described. Various salts of the alkali metals were introduced into the flame, and photographs of the spectra were obtained both by the use of a prism and a grating. The apparatus was designed so as to yield spectra of considerable intensity, and the resolving mechanism gave, in consequence, only moderate dispersion.

The photographic records show that the "continuous" spectrum emitted by sodium, potassium, and rubidium contains a large number of diffuse bands in the blue and violet region. With increased dispersion these bands appear to be partly resolved into fine lines. Apart from small differences in intensity, the appearance of these band spectra is independent of the nature of the salt of the alkali metal. Such bands were not recognisable in the flame spectra of lithium and cæsium.

The "continuous" spectrum extends into the red and ultra-red region, and the limiting wave-length at the red end increases in general with increase in the atomic weight. The approximate limiting wave-lengths are as follows: sodium, λ 6500; lithium, λ 7000; potassium, λ 8100; rubidium, λ 8600; cæsium, λ 9000.

The increased intensity shown by the "continuous" spectrum in the neighbourhood of the characteristic lines is attributed to diffusion of the light in the spectral apparatus.

The photographs of the flame spectrum of cæsium show the

second component of the principal series pair at $\lambda = 8950$, and also the pair of lines λ 7283 and 7233, which has previously only been observed in the arc spectrum. H. M. D.

A Relation Exhibited by Line Spectra. Sergius Popov (*Ann. Physik*, 1914, [iv], **45**, 147—175).—From observations of the Zeeman effect in the spectra of calcium, strontium, barium, and yttrium, the conclusion is drawn that certain pairs of triplets form members of a series which is related to the first subordinate series in much the same way that the principal series is related to the second subordinate series. H. M. D.

The Emission of Light from Metal Vapours in the Glow Discharge. L. Janicki and R. Seeliger (*Ann. Physik*, 1914, [iv], **44**, 1151—1168).—The authors describe a simple method by means of which the glow discharge can be passed through the vapours of metals. Two forms of apparatus are described, in one of which the metal to be examined is employed as cathode, in the other it serves as the anode. The discharge is started by passing a current through the tube containing hydrogen or nitrogen, the intensity of the discharge being sufficient to volatilise the metal with considerable rapidity. The foreign gas is then removed, and the glow discharge continues through the vapour of the metal.

From the results obtained with cadmium, zinc, magnesium, lead, aluminium, tin, and silver, it is found that there is a close parallelism on the one hand between the spark spectrum of the metal and that of the negative glow, and on the other between the arc spectrum and the spectrum of the positive column. The lines characteristic of the spark spectrum are shown only by the negative glow, whilst the arc lines appear only in the positive column or, at any rate, the intensity of these lines is relatively very great in the positive column. Silicon behaves similarly to the above metals, but tellurium is anomalous in that there is no analogy between the spark and negative glow spectra or between the spectra of the arc and positive column in the case of this element.

Experiments with discharge tubes containing zinc and cadmium vapour which were heated externally, gave exactly similar results to those obtained by the above-described method of experiment.

H. M. D.

Measurements in the Arc and Spark Spectrum of Mercury in International Normals. Leo Cardaun (*Zeitsch. wiss. Photochem.*, 1914, **14**, 56—68, 89—104).—The measurements were made by means of a large concave grating, the arc spectrum being obtained from a quartz mercury lamp and the spark spectrum by the use of carbon electrodes, the core of the positive electrode being filled with mercury. The wave-length data, which are recorded to 0·01, and in many cases to 0·001 Å.U., are compared with those of previous observers. The sharpness and intensity of the various lines are also indicated in the tabular record. H. M. D.

Measurements in the Ultra-violet Spark Spectrum of Copper, Aluminium, Gold, Silver, Zinc, and Carbon up to λ 1850, according to the International System. JOSEF MARIA EDER (*Zeitsch. wiss. Photochem.*, 1914, **14**, 137—147).—Measurements of wave-lengths have been made which extend from λ 2263 to λ 1853. By comparing the spectra obtained with a grating and with a quartz prism, it has been found that Hartmann's interpolation formula for the prismatic spectrum $\lambda=\lambda_0+(c/s-s_0)^{1/\alpha}$ gives results in good agreement with the wave-lengths afforded by the grating spectrum if α is equal to 1. In this formula λ_0, c, and α are constants, s_0 the zero scale reading, and s the reading which corresponds with wave-length λ. The wave-lengths recorded in the tables are given to 0·01 A.U., and where possible are compared with previous measurements.

It has been found that the carbon line λ 1930 is a double line (λ 1930·58, $i=2$; λ 1930·07, $i=8$), and is quite distinct from the aluminium line λ 1930·33. H. M. D.

Constant Differences in Line Spectra. EMIL PAULSON (*Ann. Physik*, 1914, [iv], **45**, 419—430. Compare this vol., ii, 119).—An examination of the line spectra of a large number of elements has shown the existence of groups of lines which show a constant difference of frequency. The only lines taken into consideration are those characterised by considerable intensity. Pairs of such lines in the spectra of phosphorus, scandium, titanium, iron, cobalt, germanium, bromine, krypton, yttrium, and niobium are recorded in tabular form. The wave-length data in question have been taken from Kayser's tables. H. M. D.

Regularities in the Structure of the Spectrum of Lanthanum. EMIL PAULSON (*Ann. Physik*, 1914, [iv], **45**, 1203—1208).—It is shown that the lanthanum spectrum is characterised by the occurrence of groups of six lines which show the same differences in frequency. If A is the frequency of the first member of one of these groups, then the frequencies of the other five are given by $A+2977{\cdot}86$, $A+3636{\cdot}86$, $A+4333{\cdot}66$, $A+5212{\cdot}84$, $A+6229{\cdot}16$. Tables are given showing the existence of sixteen more or less complete groups of this character. H. M. D.

A System of Wave-length Numbers in the Scandium Spectrum. EMIL PAULSON (*Physikal. Zeitsch.*, 1914, **15**, 892—894).—An investigation of the spectrum lines of the elements of the A sub-group of group III. of the periodic system has been carried out for the elements yttrium, scandium, and lutecium. In the case of yttrium it is shown that many corresponding series of four lines appear, of which if A represent the first, B, C, and D the second, third, and fourth respectively, $B=A+1846{\cdot}91$; $C=A+2251{\cdot}69$; $D=A+2456{\cdot}65$. Similar groups are found for lutecium, the relationship being $B=A+5571{\cdot}42$; $C=A+7335{\cdot}75$; and $D=A+9552{\cdot}78$. In the case of scandium, of which 440 lines appear in the arc spectrum, 203 lines can be arranged in series

of seven, the members of the series bearing the relationships $B=A+158{\cdot}77$, $\Delta_1=158{\cdot}77$; $C=A+474{\cdot}18$, $\Delta_2=315{\cdot}41$; $D=A+577{\cdot}73$, $\Delta_3=103{\cdot}55$; $E=A+717{\cdot}71$, $\Delta_4=139{\cdot}98$; $F=A+2298{\cdot}81$, $\Delta_5=1581{\cdot}10$; $G=A+2380{\cdot}75$, $\Delta_6=81{\cdot}94$. In addition to these groups other lines with a Δ value of 319·64 and 20·2 have been noticed. Tables of the wave-lengths, intensities, and differences of the lines are given in the paper. J. F. S.

Regularities in the Spectrum of Platinum. Emil Paulson (*Ann. Physik*, 1915, [iv], **46**, 698—704).—Relations of the kind described previously (compare this vol., ii, 34, 196) have also been found to occur in the platinum spectrum. In this case there is a group of ten lines which recurs, in more or less complete form, no less than thirty-four times. The corresponding members of the various groups show the same differences in frequency. The mean values of the constant differences between successive members of the groups are: 3065·72, 2006·20, 3365·33, 15·17, 3550·34, 427·52, 5318·09, 47·86, and 776·17. In this series the frequency of the members of the various groups increases from left to right. The thirty-four tables given in the paper contain 175 lines, which have been recognised as belonging to groups of this kind. H. M. D.

The Wave Number System of Ruthenium. Emil Paulson (*Physikal. Zeitsch.*, 1915, **16**, 81—84. Compare previous abstracts).—From an examination of Kayser's wave-length measurements of the lines in the arc spectrum of ruthenium, it is found that a large number of these lines fall into groups containing eighteen lines. The difference in the frequency of corresponding members of each group has a constant value. The table given by the author contains 548 lines, which fall into sixty-five more or less complete groups of this character. H. M. D.

Absorption Spectra and the Solvate Theory of Solutions. Harry C. Jones (*Zeitsch. Elektrochem.*, 1914, **20**, 552—554).—In a previously published paper (A., 1914, ii, 250) Dhar has collected a number of data of the properties of solutions which point to the existence of solvates. The present paper adds to the list published by Dhar the evidence of the absorption spectra. It is shown that a salt in a given solvent is characterised by a definite absorption spectrum. Should a salt be dissolved in a mixture of two solvents the absorption spectrum is made up of two well-defined spectra, characteristic of the dissolved substance in each solvent. If the composition of the mixed solvent is changed, the absorption spectrum does not gradually change from one form to the other, but a variation of the relative intensities of the two spectra shows itself. If the solvent A is reduced in amount in relation to the solvent B, then the spectrum corresponding with A is reduced in intensity with respect to that corresponding with B. These facts are taken to show that the solvents have combined with the dissolved substances to form solvates. The above statements are based on measurements

of the absorption spectra of neodymium chloride, uranous chloride, uranous bromide, and uranyl acetate in a large number of solvents (A., 1910, ii, 87, 172, 246, 370). Aqueous solutions of salts which show no tendency to hydrate formation have the same absorption spectra as water itself (*Zeitsch. physikal. Chem.*, 1910, **74**, 325).

J. F. S.

Relation between Absorption and Structure. I. V. A. Izmailski (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 63—100).—A theoretical paper, in which halochromy and the carbonium, quinonoid, and quinocarbonium formulæ for halochromic salts are discussed. Halochromy is regarded as of two kinds, and the following names are suggested: cat-halochromy, for cases where the carrier of the colour is the cation (chromone radicle), and an-halochromy, for those where the anion (chromaci radicle) carries the colour.

The carbonium, quinonoid, and quinocarbonium structures of halochromic salts are considered to be unsatisfactory, the principal objections being the existence of an-halochromic and cat-halochromic series, and the possibility of converting one and the same skeleton into a chromone or a chromaci radicle according to the character of the substituent groups. Against quinonoid formulæ it is urged that, with alteration of the constitutive factors, the absorption changes uninterruptedly. From the absorption and the capacity for reaction it cannot be stated where the quinonoid structure of the molecules begins and where the benzenoid structure ends. The plasticity of the molecule is clearly expressed in the existence of chromo-isomerism and chromotropy, and one and the same chromaci or chromone radicle may correspond with a greater number of colouring forms than can be foreseen from the quinonoid theory. Another weak point in this theory is that it does not attempt to find a cause of colour in any general principle applicable to other classes of compounds, but deals only with certain groups of compounds. Further, it disregards the circumstance that many compounds which are not quinones exhibit absorption similar to, and even more selective than, that of the quinones, whilst, on the other hand, quinones are known which show no characteristic absorption bands.

T. H. P.

Validity of the Rule Connecting Colour with Degree of Dispersity. Kurt Voigt (*Kolloid. Zeitsch.*, 1914, **15**, 84—85).—In the opinion of Ostwald (A., 1911, ii, 868) an increase in the degree of dispersity of a coloured colloidal solution is accompanied by a shift of the absorption maximum towards the ultra-violet end of the spectrum. It is shown that the behaviour of Congo-red is not in agreement with this statement. The addition of excess of sodium hydroxide to a solution containing Congo-red leads to an increase in the size of the particles. If the above relation holds good, the red colour should change in the direction of violet, but as a matter of fact, the change is towards yellow. In agreement with the results obtained by Pihlblad (A., 1913, ii, 2), it is found that the intensity of the absorption changes with the alteration in the

degree of dispersity in the sense that the extinction increases as the size of the colloidal particles diminishes. The fact that the colour of aniline-blue changes with the degree of dispersity in accordance with Ostwald's relation is supposed to be connected with the fact that this substance forms colloidal solutions of suspensoid character. So far as emulsoid solutions are concerned, the degree of dispersity is considered to have but little influence on the colour of dyes. H. M. D.

Theoretical Photochemistry, 1909–1913. CHR. WINTHER (*Zeitsch. wiss. Photochem.*, 1914, **14**, 19—32).—A summary of recent work on photochemical reactions. It would now seem to be established that the important factor in photochemical change is the absorbed light, and not the intensity of the incident light. H. M. D.

The Action of Light on Chlorine Water. HARRY MEDFORTH DAWSON (*Zeitsch. wiss. Photochem.*, 1914, **14**, 213—215).—On the assumption that the change in conductivity is proportional to the change in concentration of the chlorine, Benrath and Tuchel (A., 1914, ii, 447) have investigated the rate of decomposition of chlorine water under the influence of light by means of measurements of the electrical conductivity of the solution. The author contends that the above assumption is unjustifiable, for the reaction takes place in two stages, as represented by the equations (1) $Cl_2 + H_2O \rightleftarrows H^{\cdot} + Cl' + HClO$, (2) $2HClO \longrightarrow 2H^{\cdot} + 2Cl' + O_2$, and the relation between the concentration of the chlorine and that of the hydrochloric acid which determines the conductivity of the solution is regulated by the hydrolysis constant:

$$k = [H^{\cdot}][Cl'][HClO]/[Cl_2].$$

On this account the change in conductivity does not afford a measure of the change in the concentration of the chlorine, and the fact that the experimental data afford an approximately constant value for the coefficient $k = 1/t \cdot \log a/(a-x)$, does not show that the photochemical decomposition of chlorine water is a simple unimolecular change.

The fact that the addition of chlorides, and in particular of hydrochloric acid to the solution, diminishes the proportion of chlorine which is finally decomposed, can be explained quite satisfactorily in terms of the two consecutive reactions. The suggestion that the inhibiting action of these substances is due to the formation of Cl_3' ion, is inconsistent with known facts. H. M. D.

The Sensitiveness to Light of Pure Mercury Compounds. JOSEF MARIA EDER (*Zeitsch. wiss. Photochem.*, 1914, **14**, 172—176).—According to Winther (A., 1910, ii, 564), a solution of mercuric oxalate completely free from iron would be photochemically inactive. The fact that this conclusion did not agree with the author's previous observations has led to a further series of experiments with solutions prepared from carefully purified substances. These experiments show that the photochemical sensitiveness of solutions

of mercuric oxalate (mercuric chloride and ammonium oxalate) is not dependent on the presence of traces of ferric salts, but is also exhibited by the pure mercuric compound. The decomposition of the mercuric salt is mainly determined by the ultra-violet rays, but comparative observations have shown that the relative activity of the visible rays is increased if the solution contains small quantities of iron. H. M. D.

The Sensitiveness to Light of Ferric Salts. CHR. WINTHER and H. OXHOLT-HOWE (*Zeitsch. wiss. Photochem.*, 1914, **14**, 196—212).—The photochemical sensitiveness of various organic salts of iron has been examined. Solutions were prepared by mixing equimolar solutions of ammonium oxalate, succinate, tartrate, citrate, and acetate with measured volumes of ferric chloride solutions of varying concentration, and the mixtures were exposed to the action of monochromatic light of wave-length $\lambda = 436$, 405, 366, and 313 $\mu\mu$.

The results obtained show that the rate at which the ferric salt is reduced remains approximately constant during the course of the reaction. For a given concentration, the sensitiveness (measured by the ratio of the amount of substance transformed to the quantity of incident radiation) increases as the absorption-coefficient diminishes. In order to explain this, it is supposed that the solutions contain at least two substances which absorb the incident rays. One of these is photochemically sensitive, and the other not, and the latter is responsible for the major part of the absorption.

Examined from the point of view of the quantum theory, it is found that the number of reacting molecules per quantum of absorbed energy is in all cases greater than unity. H. M. D.

Colloid Chemistry of Asphalt. A. ROSINGER (*Kolloid. Zeitsch.*, 1914, **15**, 177—179).—Asphalts which dissolve in benzene, chloroform, and hydrocarbons are found to become insoluble in these liquids after being subjected in thin layers to the action of light. If solutions of asphalt in benzene or in a mixture of benzene and chloroform are poured on to glass plates and the solvent allowed to evaporate, the asphalt is found to have become insoluble even in the absence of light action. This suggests that the apparent sensitiveness of asphalt to light depends on the oxidation of the material in contact with air. When certain substances, such as safrole and eugenol, are added to the asphalt, its sensitiveness to light is increased. In presence of these sensitisers, the product obtained differs from that formed in the oxidation process, and it is supposed that the action of the light in these circumstances consists in the formation of gels by adsorption of the sensitising agents in the asphalt. H. M. D.

The Photographic Behaviour of Silver Azoimide. JULIUS BEKK (*Zeitsch. wiss. Photochem.*, 1914, **14**, 105—125).—The photographic behaviour of silver azoimide resembles that of silver chloride and bromide, but its sensitiveness to light is much less

than that of the halogen salts. The azoimide is also much more easily reduced by developing solutions, and in the unripened condition is characterised by relatively high sensitiveness to the red portion of the spectrum. The first two properties are in all probability determined to a large extent by the extreme fineness of the granular structure of the azoimide.

The darkening of silver azoimide has been shown to be accompanied by the liberation of nitrogen. Although the pure substance is highly explosive, it is found that dried emulsions of silver azoimide are quite insensitive to shock, and can be manipulated without danger.

Further experiments described in the paper have reference to the influence of ripening on the light and colour sensitiveness of gelatin and other emulsions of the azoimide and the influence of the nature of the surrounding medium on the darkening of the silver salt. H. M. D.

The Influence of Light on Colloid Systems. HUGO STINTZING (*Koll. Chem. Beihefte*, 1914, **6**, 231—296).—Various aspects of the question of the influence of light on colloid systems are discussed in detail. The phenomena of photo-crystallisation and photo-sublimation would appear to have some connexion with the action in question, although it would seem that these photo-effects cannot be observed when temperature differences are completely eliminated. On the other hand, the experiments of Alefeld (*Chem. Zeit.*, 1906, **88**, 1087) led him to assume the existence of a specific influence of light which gives rise to an increase in concentration in the part of the system which is subjected to the action of light rays.

The author's experiments, which were made with colloidal systems containing gelatin and metallic salts, silver "resinate," ferric hydroxide, silver sol, and also with molecular disperse solutions, show that local increases in concentration under the influence of light are due to inequalities in the rate of vaporisation in the insolated and non-insolated parts of the system. In the absence of such inequalities, changes in concentration do not take place, and consequently the conclusion may be drawn that there is no direct or specific influence of light on the distribution of the phases in a colloid system.

The change in the distribution resulting from local inequalities in the rate of evaporation appears to be characteristic of colloid systems. The effect is not observed with true solutions. From the results obtained with different colloid systems it would seem that the changes in concentration are more or less independent of the nature of the substances concerned, that is to say, of both the disperse phase and the dispersive medium. H. M. D.

Secondary Cathode Radiation in Gases Produced by Primary Rays of Small Velocity and the Absorption of these Rays. FRANZ MAYER (*Ann. Physik*, 1914. [iv], **45**. 1—28).—The conditions under which secondary radiation is produced by low-

speed cathode rays have been investigated by experiments with various gases. Below a certain velocity the primary rays do not produce secondary rays. This minimum velocity varies with the nature of the gas, as is shown by the following values: air, 9·5; hydrogen, 11·5; nitrogen, 11·8; carbon dioxide, 12·5; methane, 13·5; carbon monoxide, 14·5 volts. The velocity which gives rise to a maximum amount of secondary radiation was also found to depend on the nature of the gas, as shown by the following numbers: air, 130; hydrogen, 125; nitrogen, 150; carbon dioxide, 140; methane, 132; carbon monoxide, 125 volts. For primary ray velocities greater than that which corresponds with the optimum secondary radiation, the rate at which the intensity of the secondary radiation falls with increasing velocity of the primary rays depends on the radius of the gas molecules. Except in the case of hydrogen, this rate of decay is greater the smaller the molecular radius. There appears to be no connexion between the rate at which the secondary radiation diminishes and the nature of the gas if the primary rays are of smaller velocity than those corresponding with the optimum secondary effect. When the secondary radiation is at its maximum value, the quantity of radiation is proportional to the molecular weight of the gas. The behaviour of hydrogen is, however, quite abnormal, in that the quantity of secondary radiation is twelve times as large as that required by this relation.

Experiments made to determine the absorption of very slow-speed cathode rays in air have shown that the absorption of rays of velocity 0·5 to 4·2 volt is constant, and determined by the molecular cross-sectional area. H. M. D.

Adsorption of Very Hard *X*-Rays. B. Winawer (*Physikal. Zeitsch.*, 1914, **15**, 942—946).—An extremely hard Röntgen tube gives out a very penetrating radiation, which is of the nature of γ-rays in its penetrating power, and is provisionally termed *X*γ-radiation. The absorption of these rays by graphite, magnesium, aluminium, iron, copper, zinc, silver, cadmium, tin, antimony, platinum, gold, lead, and bismuth has been determined. It is shown that the mass-absorption-coefficient μ/ρ, where μ is the absorption-coefficient and ρ the density, increases continuously with the atomic weight of the metal, the values being 0·14 for aluminium and 3·2 for gold. The elements of small atomic weight absorb the radiation relatively weakly. In the case of aluminium, magnesium, and graphite, the penetrability of the *X*γ-rays approaches that of the hard γ-rays from radium. $\mu/\rho = 0{\cdot}14$ for *X*γ-rays, and 0·04 for γ-rays. In the case of the heavier elements there is a much larger difference, which increases with the atomic weight of the element. J. F. S.

Uni- and Multi-valent Lines of Aluminium, Sulphur, Chlorine, Iodine, and Nitrogen in the Canal Ray [Spectra]. J. Stark and R. Künzer (*Ann. Physik*, 1914, [iv], **45**, 29—74. Compare A., 1913, ii, 546).—In previous papers, evidence has been brought forward in support of the view that ions with different

charges (valencies) give rise to different lines in the emission spectra. Further observations have now been made on canal-ray spectra with discharge tubes containing aluminium chloride, sulphur, chlorine, iodine, and nitrogen, and on the basis of these observations an attempt is made to attribute certain lines or groups of lines in the spectra to definite carriers or centres. The conditions of electrical discharge were varied so as to obtain spectra of both the arc and the spark type.

The conclusions drawn in reference to the canal-ray spectrum of aluminium are that the doublets of the first and second subordinate series are due to positively charged univalent aluminium ions, and that the ultra-violet spark lines are to be attributed to bi- or ter-valent ions. The aluminium arc spectrum, in addition to the doublets referred to, shows others which have a smaller difference of frequency, and these also would appear to originate in univalent ions.

The observations on sulphur show that its spectrum contains four kinds of lines which can be readily distinguished. The first arc spectrum (series spectrum) is attributed to positively charged molecules, S_2, carrying a single charge, the lines of the second arc spectrum to positive univalent sulphur atoms, the sharp spark lines to positive bivalent sulphur atoms, and the diffuse spark lines to positive tervalent sulphur atoms.

The arc lines in the chlorine spectrum appear to be due to univalent chlorine atoms with a single positive charge, the sharp spark lines to positive bivalent atoms, and the diffuse spark lines to positive tervalent chlorine atoms. Although much more difficult to examine, the canal-ray spectrum of iodine is apparently similar to that of chlorine, and ionic carriers of the same type are presumably responsible for the corresponding groups of lines.

The results obtained with nitrogen permit of a distinction being made between three groups of lines. It is probable that the arc lines are due to positive univalent nitrogen atoms, the sharp spark lines to positive bivalent atoms, and the diffuse spark lines to positive tervalent atoms.

In arriving at the above results, the authors attach considerable importance to the relative intensities of the lines which show the Doppler effect and those which do not under the different conditions of electric discharge. H. M. D.

The Röntgen Spectrum of Platinum. H. Seeman (*Physikal Zeitsch.*, 1914, **15**, 794—797).—The Röntgen ray spectrum of platinum has been photographed and measured. Hard bulbs were used, and lithium-glass windows. It is shown that the broad continuous bands and a large number of lines recorded by previous observers are made up of many fine lines. A photograph of the spectrum is appended to the paper. J. F. S.

Superficial Burn Produced by an Unknown Radiation. Charles A. Doremus (*J. Amer. Chem. Soc.*, 1915, **37**, 549—551).—During an experiment in which a calcium zinc alloy was heated in

a furnace with lamp-black, the author suffered superficial burns, the effect being produced through his clothes. The burns resembled those produced by *X*-rays and radium radiation. The experiment was repeated, a sheet of lead perforated with five holes being interposed between a Cramer *X*-ray "X" plate and the furnace. The plate, on being developed, showed the five holes in the lead covering, and thus confirmed the diagnosis of the nature of the burns. When coke, charcoal, or gas carbon was used with the alloy instead of lamp-black, photographic evidence of the radiation could not be obtained. E. G.

Influence of the Edges of Metal Leaves on the Penetrability of Radioactive Rays. ALFRED IMHOF (*Zeitsch. wiss. Photochem.*, 1914, **14**, 171—172).—A photographic plate was exposed to the rays emitted by a circular disc cast from gypsum mixed with uranium oxide. A number of concentric rings of tin foil, 0·02 mm. thick, were placed between the plate and disc, the ring with the smallest inner radius being next to the photographic plate which was covered with a thin sheet of note-paper. The developed plate shows a series of sharp concentric rings, although the varying thickness of the tin foil is without appreciable influence on the photographic effect. These rings correspond with the inner edges of the successive sheets of metal. H. M. D.

Velocity of Ionisation at Low Temperatures. ALEXANDER ROBERT NORMAND (T., 1915, **107**, 285—290).—The direct determination of the velocity of ionisation has not hitherto been attempted, and measurements have therefore been made by the following method. A solution of potassium iodide in ethyl alcohol was cooled at the f. p. of methyl alcohol (−97·8°) or of ethyl alcohol (−117·6°) until its temperature and conductivity were constant. An equal quantity of the solvent, cooled to the same temperature, was then quickly added, and the solution well stirred. If the additional ionisation due to dilution should proceed slowly enough, the conductivity of the solution immediately after dilution would be half that of the original solution, and would then gradually rise to the value of the conductivity of the solution at half the initial concentration, and a measurement of the velocity of ionisation would be obtainable from a curve showing the variation of the conductivity with time.

The specific conductivity of solutions of potassium iodide (1 gram) in ethyl alcohol (100 grams) has been determined between −100° and +25°. The conductivity of the solvent alcohol at −100° to −80° was so small as to be negligible. It was observed that the temperature-coefficient of conductivity was much greater at the lower than at the higher temperatures.

A study of the effect of dilution on the conductivity showed that at −98° and even at −118° ionisation is complete in less than three minutes, and from an examination of the time-curves it seemed probable that ionisation is completed within one minute at −118°. It is calculated that at the ordinary temperature ionisation is completed in less than 1/100th of a second. E. G.

Does an Ionisation of a Mixture of Chlorine and Hydrogen Occur when it is Illuminated and does a Reaction Occur in the Same Mixture when it is Ionised by Röntgen Rays? M. Le Blanc and M. Vollmer (*Zeitsch. Elektrochem.*, 1914, **20**, 494—497).—As the result of a number of experiments it is shown that a mixture of chlorine and hydrogen, when illuminated by an Osram lamp of 25—100 candle-power, is not ionised to a measurable extent, and that the results of Kümmell (A., 1911, ii, 796) must be explained by a bad insulation of his apparatus. In the present experiments a quantity of hydrogen chloride amounting to 0·56 c.c. at 20° was formed during an illumination of fifty seconds' duration. When exposed to Röntgen rays, 0·03 c.c. of hydrogen chloride was produced in sixty seconds, which means that a single electron can at most bring 10^4 molecules into reaction, and not 10^{12} as has been previously supposed. J. F. S.

Electron Emission During Chemical Reactions. G. Just and F. Haber (*Zeitsch. Elektrochem.*, 1914, **20**, 483—485).—Using an apparatus similar to that previously employed (A., 1910, ii, 572) the electron emission of potassium, when submitted to light and during its reaction with thionyl chloride, has been measured. The illumination was effected by means of a candle or an arc. It is shown that when the reaction is carried out in the light the electron emission is much greater than when it is effected in the dark. The sum of the photo effect of potassium alone, and that of the illuminated reaction is always less than that of the illuminated reaction. It is also shown that the action of hydrogen chloride and iodine vapour on the metals aluminium, copper, and silver, is accompanied by an electron emission. This, however, does not take place until the metals are heated. In the case of aluminium it commences at 160° and increases rapidly with temperature, becoming very large at 240°. The electron emission commences when the pressure of the reacting gas has reached a few thousandths of a mm., and it increases very rapidly with increasing pressure. The unipolar character of the reaction ceases when the vigour of the reaction and strength of the effect become too large. In any case if a positive potential is applied to the metal the electrometer shows no motion. J. F. S.

Adsorption and Precipitation of the Radio-elements. Fritz Paneth (*Physikal. Zeitsch.*, 1914, **15**, 924—929).—A theoretical paper in which it is shown that the precipitation of radio-elements along with other substances can be explained by adsorption. It is also shown that those radio-elements are readily adsorbed the analogous compounds of which are sparingly soluble in the solvent. Thus in *N*-hydrochloric acid barium sulphate adsorbs 88% of radium sulphate, but silver chloride does not adsorb radium chloride at all. This points to the view that the anion and cation even in the solid state possess free valencies, and that the sparing solubility of a precipitate is to be attributed to the holding together of these

valencies. This view, with the fact that a kinetic exchange of atoms occurs at the surface of an absorbent, is capable of explaining the adsorption rule, and also the fact that radio-element compounds are precipitated at concentrations far removed from that at which the solubility product is exceeded. J. F. S.

The End Products of Radioactive Disintegration Series. K. FAJANS (*Zeitsch. Elektrochem.*, 1914, **20**, 449—450).—A theoretical paper in which the final products of disintegration of the radium, thorium, and actinium series are discussed. In the case of the radium series it is well known that lead constitutes the final product, and in the other two series, making use of the rules (1) that the product of a radioactive disintegration, which is accompanied by the emission of an α-particle, has a position in the periodic system two groups to the left of that occupied by its direct parent, and (2) the product of a disintegration accompanied by a β-ray emission occupies a position one group to the right of its parent, it is shown that the end-products are also lead. The various lead isotopes are also shown to have different atomic weights, and the author is of the opinion that other varieties of lead exist. A discussion of the results of atomic-weight determinations of lead from different sources, to be published shortly by Richards and Lembert, follows. In connexion with this, the view is expressed that lead from thorium is less stable than lead from uranium, and that it constitutes the first of a series of disintegrating substances which are just so stable as not to be recognised as unstable by radioactive measurements. J. F. S.

The Preparation of Radium-*D* in Visible Quantity and its Chemical Identity with Lead. G. VON HEVESY and F. PANETH (*Ber.*, 1914, **47**, 2784—2786).—The remarkably close similarity between isotopic elements has been recognised from the fact that hitherto all attempts to separate them have been futile. By taking the emanation from 1 gram of radium (element), allowing it to decompose in a sealed quartz vessel, and then dissolving in nitric acid, it has been found possible by electrolysis to isolate radium-*D* or radium-*D* peroxide, according to the conditions of experiment, in visible quantities of approximately 0·005 mg.; the activity of the product indicated the purity of the radium-*D* obtained. The comparison of the *E.M.F.* of a combination radium-*D* peroxide–radium-*D* nitrate with that of the combination lead peroxide–radium-*D* nitrate and the effect of the addition of lead ions to each, showed the actual electrochemical identity of radium-*D* and lead.

By analogy, therefore, it is highly probable that isotopic elements generally are chemically identical, and that identity of the nuclear positive electric charge (Rutherford and Andrade, A., 1914, ii, 408) is the conditioning factor for the chemical identity of two elements, the surrounding ring of electrons not being of necessity the same. D. F. T.

The Average Thorium Content of the Earth's Crust. J. H. J. POOLE (*Phil. Mag.*, 1915, [vi], **29**, 483—489).—The composite rock mixtures employed in a previous investigation of the radioactivity of terrestrial surface materials (Joly, A., 1912, ii, 1032) have been used in the investigation of the average thorium content. The residue, left after fusion with a mixture of alkali metal carbonates and treatment with water, was dissolved in hydrochloric acid, and the solution set aside for some days to allow of the accumulation of the products of disintegration of thorium. The thorium emanation was then boiled off in a constant current of air, which subsequently passed through an electroscope in which the rate of leak was determined.

In calculating a mean value from the observed results, a weight proportional to the number of rocks in the several mixtures may be assigned to the individual values, and in this way it is found that eighty-six acid rocks give a mean value of $2{\cdot}08 \times 10^{-5}$ gram thorium per gram. In the same way, the value obtained for forty-eight intermediate rocks is $1{\cdot}64 \times 10^{-5}$, and for fifty-six basic rocks $0{\cdot}56 \times 10^{-5}$. The thorium content decreases, therefore, in passing from acid to basic rocks. The same result was found for the radium content, but the ratio of radium to thorium is not constant, although in nearly all cases it lies within the limits 1·3 and $2{\cdot}7 \times 10^{-7}$. In general, the ratio increases in passing from the acid to the basic rocks.

The general mean obtained for the thorium content of the above method is $1{\cdot}50 \times 10^{-5}$. The data for a number of miscellaneous rocks were not made use of in the deduction of this value.

H. M. D.

Isotopic Elements. K. FAJANS (*Physikal. Zeitsch.*, 1914, **15**, 935—940).—The relationships of isotopic elements are considered in the present paper. It is shown that the isotopic elements and their corresponding compounds are soluble in one another in the solid form in all proportions. From this it follows, and has also been shown experimentally, that the normal potential and molecular solubility of the isotopes and their compounds are identical, and consequently the behaviour of a mixture of isotopes, in respect of their electrochemical behaviour and crystallisation, is at once obvious, the main result being that, in an equilibrium mixture, the ratio of the concentration of the isotopes must be the same in all phases. This at once leads to the fact that isotopes are non-separable. In the case of thorium-*B* and lead it is shown that the isotopes freely mix with one another by diffusion, which means that the osmotic properties of an element are not influenced by the presence of its isotopes. The diffusion of isotopes into one another is accompanied by a decrease of free energy. This implies that in their chemical mass relationships the isotopes are to be regarded as independent substances, and that, strictly, the law of mass action and the Nernst potential formula must be applied to each isotope separately, but when the salts of the isotopes have the same solubility correct results are obtained if the mixture of isotopes is

regarded as a single substance the concentration of which is the sum of the concentrations of the individual isotopes. This, however, does not imply, as stated by Hevesy and Paneth (this vol., ii, 130), that the isotopes are entirely replaceable by one another. This would only be the case if it were possible, in a system in equilibrium, to replace a portion of the atoms of one isotope by atoms of another in a single phase without affecting the composition of the other phases. This has been shown above to be impossible, and consequently there is no reason for any change in the conception of a chemical individual. J. F. S.

Radioactivity of the Deposits of the Eugenie and Ekaterine Springs in Borschom. E. BURKSER (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 21—25).—These springs form reddish-brown deposits consisting principally of hydrated ferric carbonate, together with 4·7% and 34·1% respectively of clay insoluble in dilute hydrochloric acid. In both cases radium and thorium (or mesothorium) emanation are present, the proportions found being $10·08 \times 10^{-12}$ and $26·2 \times 10^{-5}$ gram respectively per gram for the deposit of the Eugenie spring, and $17·89 \times 10^{-12}$ and $3·26 \times 10^{-5}$ gram respectively for that of the Ekaterine spring. The water of the former spring contains $0·02 \times 10^{-9}$ gram of radium per litre, and that of the latter $0·07 \times 10^{-9}$ gram; the thorium-contents of the two waters are almost identical, and do not exceed $7·02 \times 10^{-4}$ gram per litre.

T. H. P.

Dielectric Constants of Some Organic Solvents at their Melting or Boiling Points. JOHN DOUGLAS CAUWOOD and WILLIAM ERNEST STEPHEN TURNER (T., 1915, **107**, 276—282).—In connexion with investigations on molecular complexity (Turner and Pollard, T., 1914, **105**, 1751) it was desired to know the dielectric constants of solvents at either their m. p. or b. p., and determinations have therefore been made, at one or both of these temperatures, with benzene, naphthalene, and *cyclo*hexane; *o*- and *p*-chloronitrobenzene and *p*-dichlorobenzene; *p*-chloro-, bromo-, and iodo-toluenes, and *p*-nitrotoluene; chloroform and bromoform; *p*-toluidine, diphenylamine, and pyridine; veratrole; benzil; *iso*amyl alcohol and dimethylethylcarbinol; methyl succinate and methyl *p*-toluate.

The results have shown that the decrease of the dielectric constant with the temperature is either linear or nearly so. The temperature-coefficient of the dielectric constants of hydrocarbons is very small; for benzene it is 0·00066 and for *cyclo*hexane 0·00078, whilst for bromoform, which has the next lowest coefficient of the substances examined, it is 0·00255. The highest temperature-coefficients obtained were those of *iso*amyl alcohol, 0·00801, and dimethylethylcarbinol, 0·00454. Calculations from existing data have shown that there is no connexion between molecular complexity and the temperature-coefficient of the dielectric constant.

The dielectric constant is greatly increased by the introduction of a nitro-group into a hydrocarbon or a halogen derivative of a hydrocarbon. The effect of halogenation on the dielectric constant

varies according as the halogen occupies the ortho- or the para-position. Of mono-halogen derivatives, the chloro-derivative usually has the highest, and the iodo-derivative the lowest dielectric constant. The dielectric constants of *iso*amyl alcohol and dimethylethylcarbinol at 20° are 15·0 and 11·5, but at their b. p.'s the order is reversed, the values being 5·7 and 7·9 respectively. E. G.

The Behaviour of the Electrical Resistance of Metals at Low Temperatures. HANS SCHIMANK (*Ann. Physik.*, 1914, [iv], **45**, 706—736).—According to Nernst, the variation of the electrical resistance of a metal with the temperature runs more or less parallel with the variation of the energy content. In order to obtain further evidence on this point, measurements of the electrical resistance have been made between room temperature and that of boiling hydrogen. The metals examined were lead, cadmium, gold, silver, zinc, copper, cobalt, nickel, and iron. The resistance of coils of wire of the various metals was obtained by measuring the fall of potential along the wire which was placed in the interior of a hollow copper block immersed in the cooling bath.

At low temperatures the influence of impurities on the electrical resistance of metals is very considerable, and according to Nernst (A., 1910, ii, 263; 1911, ii, 368, 464, 466, 964) the resistances r_1 and r_2 of two samples of metal are connected by the relation $r_1=(r_2-a)/(1-a)$, where a is a constant which depends on the purity and homogeneity of the metal. The results obtained by the author afford support for the validity of this relation, and by determination of the constant a the equation is applied to obtain from the observed values of the resistance, values which would correspond with the pure metal.

The curves obtained by plotting the "reduced" resistances against temperature show that between 20° and 80° (absolute) the variation of the resistance with the temperature runs parallel with the values of $\beta\nu$ for the respective metals (β being a constant and ν the atomic frequency of the metal in terms of the quantum theory).

The dependence of the electrical resistance on the previous history of the metal and on differences in the crystalline structure is also discussed on the basis of special experiments which were made to elucidate the influence of these factors. H. M. D.

Electrical Excitability and Conductivity of Liquid Insulators [Benzene, Light Petroleum, etc.]. D. HOLDE (*Ber.*, 1914, **18**, 3239—3257).—It is well known in laundry works that when woollen goods are moved about in benzene the former become positively and the latter negatively charged, and that, on approach of the hand, a spark discharge may occur, thereby causing ignition of the liquid. To obviate this danger, Richter has proposed the addition of magnesium oleate, the action of which probably depends on an increase in the specific conductivity of the benzene. It is further found that liquid insulators, such as ether, light petroleum, and benzene, can acquire a charge amounting to several

thousand volts when pumped through metal tubes, and to minimise the danger of fire in such cases Richter has proposed that the tubes, reservoirs, etc., should be earthed. These measures have been criticised by Dolezalek, who considers that in the case of good insulators the charge cannot be sufficiently rapidly dissipated in this manner.

The author has therefore determined the conductivity of various samples of benzene and light petroleum by Siemens' discharge method, performed a number of experiments on the potential acquired by liquid insulators when pumped through metal tubes, and studied, also, the effect of static charges. He is led to the following conclusions: The specific conductivity of different specimens of laboratory benzene and light petroleum is 10^{-14} to 10^{-15}. The degree of electrical excitement of a liquid of low electrical conductivity caused by passage under pressure through narrow metal tubes depends, other things being equal, on the conductivity of the liquid, which is influenced by temperature, moisture, and other impurities. The electrical charges acquired by liquid insulators (benzene or light petroleum) by passage through narrow tubes are instantly dissipated under the conditions of the experiments by earthing the receivers when the conductivity is not less than 10^{-15}. This effect does not appear to depend on the electrical conductivity of the liquid, but rather on the mechanical movement experienced by the mobile benzene when forced into the receivers, and also on the convection currents, whereby all the charged particles are speedily brought into contact with the walls of the vessel. In this connexion, it is therefore recommended that the discharge pipe should be brought close to the bottom or to the sides of the tank.

The electrical excitability of liquid insulators can be diminished not only by addition of soap, but also of alcohol or acetic acid, which also increases the conductivity. H. W.

Neutral Salt Action and the Condition of Ions in Solution. II. G. Poma (*Zeitsch. physikal. Chem.*, 1914, **88**, 671—685. Compare A., 1914, ii, 440).—The influence of the addition of various quantities of neutral salts on the hydrogen potential of hydrochloric acid, hydrobromic acid, acetic acid, formic acid, lithium hydroxide, and potassium hydroxide, and the silver potential of silver nitrate and ammonio-silver nitrate has been determined. The results are expressed in the form: $n = H'_0/H'$. The influence of neutral salts on the apparent dissociation of the acids is the same as that previously observed for the copper salts (*loc. cit.*). If the various cations are arranged in order of their action on the dissociation, the order obtained will be the same as that obtained for the copper salts. In the case of the copper salts, however, the influence of the neutral salt decreases with decrease of concentration of the substrate, whereas in the case of acids the influence is independent of the concentration, except in the case of solutions containing very small concentrations of hydrogen ions. In these cases it is possible to notice a variation of n, which, however, is generally so small as

to fall within the limits of experimental error. In the case of the silver salts the results differ from those observed for the copper and hydrogen ions except in the case of ammonio-silver nitrate, where they are similar. The results of the investigation do not make it possible to state that the ions are capable of exercising a dissociating influence on the undissociated molecules. J. F. S.

The Surface Potentials of Solutions in Contact with Insulators. G. Borelius (*Ann. Physik*, 1914, [iv], **45**, 929—940).—A method is described by means of which the author has measured the potential differences at the surface of aqueous solutions in contact with glass and with paraffin.

The results obtained with a glass surface indicate that the contact potential is largely determined by the hydrogen-ion concentration. For hydrochloric acid solutions of varying concentration the surface potential increases as a linear function of the logarithm of the hydrogen-ion concentration (x) as expressed by the equation $P = 254{\cdot}5 + 58{\cdot}4 \log x \times 10^5$ millivolt. The addition of a neutral salt such as potassium chloride is without appreciable effect on the surface potential, whilst potassium hydroxide reduces the potential difference, but the reduction does not bear any simple relation to the hydroxyl-ion concentration.

The potential difference at a paraffin surface is increased on the addition of electrolytes, whether acid, basic, or neutral. For a given electrolyte, the increase is proportional to the logarithm of the electrical conductivity of the solution as represented by the equation $P = P_0 + k \log x \times 10^5$, in which k is a constant determined by the nature of the dissolved electrolyte, and x is the conductivity. This equation could not, however, be tested in the case of very dilute solutions, for these were found to exhibit widely varying contact potentials. For $N/25$-solutions the observed values of P vary from 34 millivolts in the case of sodium carbonate to 90 millivolts for hydrochloric acid. H. M. D.

Silver Voltameters. G. A. Hulett and G. W. Vinal (*J. Physical Chem.*, 1915, **19**, 173—192).—A comparison has been made of various types of silver voltameters and the methods of using them. The type of voltameter mainly concerned is the porous-cup type. It is shown that after the porous cups have been brought into equilibrium with the electrolyte, as shown by acidity tests, all voltameters, irrespective of the shape or size of the porous cup, are in excellent agreement. In the acidity tests methyl-red has been used in preference to the more sensitive iodoeosin, because it is much simpler to use and gives sufficient accuracy. It is found that when the voltameter cups are allowed to remain filled with water, a progressive solution of the silver deposit takes place. This solution is shown to be a galvanic action, and takes place even in conductivity water. Hence it is shown that the results obtained are more accurate if the silver deposit is washed and dried immediately the experiment is finished. J. F. S.

Electrolytic Valves. GÜNTHER SCHULZE (*Zeitsch. Elektrochem.*, 1914, **20**, 592–597).—A theoretical explanation of valve action and the nature of an electrode which exercises this action is given. The surface of the electrode is supposed to be covered by (*a*) a non-porous oxide layer of molecular thickness, which in the case of aluminium protects the electrode from the action of the liberated oxygen; (*b*) a layer which is probably a gas layer in the pores of an oxide layer; and (*c*) a porous layer of oxide filled with electrolyte. The formation of an aluminium valve electrode is considered by the author to take place as follows: When a freshly polished aluminium electrode is dipped in the electrolyte, a thin layer (*a*) is at first formed; this insulates, but in consequence of its molecular thickness is soon pierced by the anions, which thus reach the metal and are discharged, forming a new non-porous oxide layer. This process continues, so that the porous layer *b* is produced. Then the resistance to the passage of the anions becomes so great that the anions cannot pass to the electrode, so that they are discharged in *b*, and the electrons alone travel to the metal, and *b* in this way becomes filled with oxygen. Further oncoming anions now cannot enter the pores, their charge is torn from them, and electrons alone reach the electrodes, whilst the oxygen is repelled and liberated in the gaseous form at the surface of the porous layer. J. F. S.

Electrochemical Reactions Occasioned by the Passage of a Current Across the Boundary of a Gas into an Electrolyte. F. HABER and A. KLEMENC (*Zeitsch. Elektrochem.*, 1914, **20**, 485–488).—The present experiments have been carried out with the object of determining the rôle of the electrode in the oxidation or reduction of depolarisers. Sulphuric acid of various strengths has been electrolysed in a vessel so constructed that it could be evacuated, and one electrode could be fixed a few mm. above the liquid. The experiments were carried out at a series of temperatures, and in the case where the cathode was in the gas more hydrogen was obtained than the Faraday law demands, whilst persulphuric acid and Caro's acid were formed in the solution. The formation of these substances and of hydrogen peroxide was more noticeable when the anode was in the gas. In all cases a voltage of 600 was employed. It is shown that the concentration of active oxygen (Caro's acid, persulphuric acid, and hydrogen peroxide) increases with increasing concentration of the sulphuric acid up to 45%, when it begins to fall off, and at 75% sulphuric acid there is no formation of these substances. A considerable cooling diminishes the amount of these substances, although here the amount produced is still in excess of that demanded by Faraday's law. If oxygen is led into the anode chamber up to a pressure of 131 mm. there is also a decrease in the amount of active oxygen. An increase in the length of time or in the current strength does not affect the result to a marked extent. The results lead to the view that at the electrode a strong oxidising product is formed from the water. This is taken up by the solution, and is sufficiently stable to effect the oxidation

of the sulphuric acid, forming persulphuric acid, Caro's acid, and hydrogen peroxide. J. F. S.

Electrolytic Processes at Diaphragms. I. Neutrality Changes. ALBRECHT BETHE and THEODOR TOROPOV (*Zeitsch. physikal. Chem.*, 1914, **88**, 686—742).—In an earlier publication (Bethe, *Centr. Physiol.*, 1909, **23**, No. 9), it is shown that when a current is sent through a neutral electrolyte, which is divided by a membrane the solution becomes acid on the negative side of the diaphragm and alkaline on the positive side. The rate at which these changes are brought about depends on the nature of the electrolyte. Further, if in a neutral or alkaline solution the anion shows an increase in concentration on the cathode side of the diaphragm, the change can be made to occur on the anode side by making the solution acid. Water also moves in the same direction as that in which the concentration increases. The present paper deals with the above-mentioned changes. A theory of the process is considered, and a large number of experiments carried out, which confirm it. The rate at which the solution becomes acid or alkaline has been measured for diaphragms made of collodion, parchment, gelatin, animal membranes (pig's bladder), gold beater's skin, egg-albumin, agar-agar, gas-carbon, and alumina. The influence of concentration of the electrolyte, temperature, thickness of the membrane, and nature of the salts used have been determined in every case. The method consists in passing a current through a solution in a cell, divided by a diaphragm, and noting by means of a microscope the time required for a solution of rosolic acid to show a definite acid or alkaline colour change. It is shown that the magnitude of the change in the concentration of hydrogen ion on either side of the diaphragm can amount to 10^3 times the original concentration. The disturbance time, that is, the time required to bring about a definite change in the neutrality, is dependent on the potential applied to the cell. The time-potential curve is practically a hyperbola, and can be regarded as made up of two factors, the real disturbance time, and the time required for a diffusion so that the effect becomes visible. The minimum potential to bring about the change is 1 volt when parchment diaphragms are used; in other cases it is higher. The thickness of the diaphragm is without influence. The disturbance time decreases with increasing concentration of the electrolyte when the potential remains constant, whereas the quantity of electricity necessary to bring about the change increases. The neutrality disturbance takes place more rapidly the higher the temperature, and the curve obtained is similar to the temperature curve of viscosity of water $\times$ (dissociation of water)$^{\frac{1}{2}}$. In the case of gelatin the time of disturbance increases rapidly as the melting point is approached, but no disturbance occurs after the gelatin has melted. The time of disturbance is dependent on the nature of the electrolyte. The anions have the same influence in all the cases examined, the tervalent ions having the greatest influence, and the univalent ions the least, the order of their

influence being citrate ion$'''$, PO_4''', C_2O_4'', SO_4'', I', Br', Cl', NO_3'. The influence of cations is the reverse of that of the anions, the univalent ions having the greatest effect. With parchment, gelatin, and pig's bladder membranes the order is $NH_4^{\cdot}$, $Li^{\cdot}$, $K^{\cdot}$, $Cs^{\cdot}$, $Na^{\cdot}$, $Mg^{\cdot\cdot}$, $Ba^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, $La^{\cdot\cdot\cdot}$, $Co(NH_3)_6$. In the case of collodion and insoluble gelatin, changes in the position of the uni- and bi-valent ions are observed, but in general the order is maintained. In the case of gelatin a change in the position of the disturbance is observed when multivalent cations in combination with univalent anions constitute the electrolyte. Alongside the disturbance of the neutrality a diffusion of water takes place, generally in the direction from anode to cathode. This is influenced by temperature, potential, and the nature of the anode, in the same way as the neutrality disturbance. If the position of the neutrality disturbance changes, the electroendosmosis changes its direction. The electroendosmosis is proportional to the current, and the curve, representing the time in which equal quantities of water diffuse at different temperatures, is the same as the viscosity-temperature curve of water. The similarity of the conditions accompanying the electroendosmosis and the neutrality disturbance and many other points indicate that the cause of the neutrality disturbance is to be found in the existence of electric charges on the walls of the capillaries in the diaphragms. J. F. S.

The Dilution Law at High Concentrations. CHARLES A. KRAUS (*Zeitsch. Elektrochem.*, 1914, **20**, 524—529).—Polemical. In the first place a claim for priority over Sachanov and Prscheborovsky (A., 1914, ii, 92), and secondly a criticism of the use made by Sachanov (*Zeitsch. physikal. Chem.*, 1913, **83**, 144) of the viscosity determinations of Sprung (*Ann. Phys. Chem.*, 1876, [ii], **159**, 1) in correcting electrical conductivity determinations for the influence of viscosity (compare also Kraus and Bray, A., 1913, ii, 914). J. F. S.

Abnormal Electrolytic Dissociation. A. SACHANOV (*Zeitsch. Elektrochem.*, 1914, **20**, 529—537).—An answer to Kraus (see preceding abstract) and a résumé of the various regularities observed in cases of abnormal electrolytic dissociation, and the hypotheses which have been put forward to explain the abnormality. J. F. S.

The Equilibrium : Hydrogen Ion–Water–Alcohol. HEINRICH GOLDSCHMIDT (*Zeitsch. Elektrochem.*, 1914, **20**, 473—479).—It is shown that if the equivalent conductivity of an aqueous alcoholic solution of an acid is known for three different water concentrations, the value of r, the equilibrium constant of the system, hydrogen-ion–water–alcohol, can be calculated. A series of experimental results are given, which include equivalent conductivities λ_∞ and $\lambda_{0\cdot1}$ for hydrochloric, 5-sulphosalicylic, picric, trichloroacetic, trinitrobenzoic, trichlorobutyric, dichloroacetic, and salicylic acids.

The equilibrium constant for alcohol with varying water-content is calculated from the conductivities of the acids mentioned.

J. F. S.

Mobility of Some Multivalent Cations in Water. A. HEYDWEILLER (*Zeitsch. physikal. Chem.*, 1915, **89**, 281—286).—A theoretical paper. The author has deduced the approximate ionic conductivities of the cations Gl$^{\cdot\cdot}$, Al$^{\cdot\cdot\cdot}$, Cr$^{\cdot\cdot\cdot}$, Mn$^{\cdot\cdot}$, Fe$^{\cdot\cdot}$, Fe$^{\cdot\cdot\cdot}$, Ni$^{\cdot\cdot}$, Co$^{\cdot\cdot}$, La$^{\cdot\cdot\cdot}$, Sm$^{\cdot\cdot\cdot}$, and Th$^{\cdot\cdot\cdot\cdot}$ by using the equivalent conductivity at infinite dilution. The latter value has been obtained by the Kohlrausch method of plotting the equivalent conductivity against the linear concentration, that is, the cube-root of the concentration, and extrapolating for the value at infinite dilution. The equivalent conductivities were thus obtained for the chloride nitrate, bromide, and chlorate of the above-mentioned cations, and with the exception of glucinum concordant results were obtained. The calculations lead to the following ionic conductivities at 18°: $\frac{1}{2}$Gl$^{\cdot\cdot}$, 27·9; $\frac{1}{3}$Al$^{\cdot\cdot\cdot}$, 40·4; $\frac{1}{3}$Cr$^{\cdot\cdot\cdot}$, 44·9; $\frac{1}{2}$Mn$^{\cdot\cdot}$, 44·1; $\frac{1}{2}$Fe$^{\cdot\cdot}$, 45·3; $\frac{1}{3}$Fe$^{\cdot\cdot\cdot}$, 61·2; $\frac{1}{2}$Ni$^{\cdot\cdot}$, 44·2; $\frac{1}{2}$Co$^{\cdot\cdot}$, 43·0; $\frac{1}{3}$La$^{\cdot\cdot\cdot}$, 49·7; $\frac{1}{3}$Sm$^{\cdot\cdot\cdot}$, 53·5; $\frac{1}{4}$Th$^{\cdot\cdot\cdot\cdot}$, 23·5. The values for $\frac{1}{2}$Mn$^{\cdot\cdot}$, $\frac{1}{2}$Ni$^{\cdot\cdot}$, and $\frac{1}{2}$Co$^{\cdot\cdot}$ are compared with those of Althammer (*Diss.*, Halle, 1913) obtained directly, and differ 1—3 units from these, showing that the values are only approximate, and have a probable error which may exceed 5%.

J. F. S.

The Dissociation Constants of Carbonic Acid. L. MICHAELIS and P. RONA (*Biochem. Zeitsch.*, 1914, **67**, 182—192).—The method employed is that suggested by Michaelis for the determination of the dissociation constant of weak acids, namely, the electrometric measurement of the hydrogen-ion concentration by a known mixture of the acid in the presence of its sodium salt, which was obtained by the addition of measured quantities of $N/2$-sodium carbonate solution to measured quantities of a N-hydrochloric acid diluted with water, and making up this mixture to a definite volume. Electrodes devised by Michaelis for measurement of [H$^{\cdot}$] concentrations of liquids containing carbon dioxide were employed. The value of the dissociation constant found by this method was $4{\cdot}4 \cdot 10^{-7}$. By applying this constant to a liquid with the same amount of sodium as the blood, it was calculated that the dissociation grade of sodium hydrogen carbonate in this fluid is 0·6.

S. B. S.

The Dissociation Constant of β-Hydroxybutyric Acid. L. MICHAELIS and T. GARBENDIA (*Biochem. Zeitsch.*, 1914, **67**, 193—197).—From electrometric measurements of the [H$^{\cdot}$] concentration in mixtures of this acid and its sodium salt, the dissociation constant was found to be $3{\cdot}86 \cdot 10^{-5}$. The dissociation grade of sodium hydroxybutyrate in a solution containing 0·85% sodium chloride (as in blood) was calculated as 0·72, whilst in a solution containing 2% sodium chloride (as in urine) it was calculated as 0·64. A method is given for applying these numbers to determine the proportion of β-hydroxybutyric acid free (that is, not combined as sodium salt) in blood and in urine.

S. B. S.

The Isoelectric Point of Carbohæmoglobin and of Reduced Hæmoglobin. L. MICHAELIS and Z. BIEN (*Biochem. Zeitsch.*, 1914, **67**, 198—202).—For both these substances the isoelectric point was found to be $1{\cdot}7 . 10^{-7}$. The method of electrocataphoresis with the employment of phosphate mixtures was used, and in the case of reduced hæmoglobin a slight modification of the ordinary apparatus, which is described and figured, was devised to prevent oxidation during the determinations. S. B. S.

Electrolysis of Glass. A. SPERANSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 52—58. Compare Warburg, A., 1884, 1241; Le Blanc and Kerschbaum, A., 1910, ii, 481; Heydweiller and Kopfermann, A., 1910, ii, 685; Schulze, *Ann. Physik*, 1912, [iv], **37**, 435, and 1913, [iv], **40**, 335).—In previous work on the electrolysis of glass, mercury, or its alloys, or fused salts have been employed as anode. The author has replaced these by concentrated sulphuric acid, and has investigated the electrolysis of the following kinds of glass: Jena, "R," hard, lead, and soda. Under these conditions the first four exhibit behaviour similar to that observed by Warburg in the electrolysis of soda-glass with a mercury anode. The soda-glass, on the other hand, becomes opaque, and its electrical conductivity at first falls and later increases rapidly until it exceeds the initial value.

The use of sulphuric acid as cathodic liquid facilitates the investigation of the products of electrolysis of the glass. T. H. P.

The Structure of Electrolytically Deposited Copper. A. SIEVERTS and W. WIPPELMANN (*Zeitsch. anorg. Chem.*, 1915, **91**, 1—45. Compare Faust, A., 1912, ii, 1173).—The experiments deal with copper deposited under different conditions of concentration, acidity, and current density, and with the influence of colloids on the structure. The anode used is a horizontal ring of copper wire, enclosed in parchment-paper. The cathodes are of iron, varnished except on the under surface, directed towards the anode. A central Witt's stirrer is provided. Most of the deposits separate readily from the cathode, and are obtained in the form of sheets 0·1—0·3 mm. thick. For transverse examination with the microscope these are clamped between pieces of pure copper, and sawn through. The sections are deeply etched without polishing.

Solutions of copper sulphate containing sulphuric acid yield first a very finely crystalline deposit, which does not adhere to the cathode. V-shaped crystallites then grow outwards in an approximately perpendicular direction. Their size at first diminishes with increasing current density, but after a certain limit is reached, it again increases, at the same time becoming less regular. At very high current densities the deposit becomes very irregular and porous. All changes which tend to equalise differences of concentration displace this limit towards higher current densities. Increased acidity and, to a less extent, increased viscosity due to addition of glycerol or inorganic salts, produces the same effect. Neutral sulphate solutions yield a brittle deposit, in which cuprous

oxide particles are enclosed between the crystallites. Acid solutions of the nitrate yield large, dendritic growths.

Small additions of colloids render the deposits brittle without appreciably altering the microscopic structure. With larger additions the crystals become smaller, and dark, intercrystalline layers are seen on etching. These layers are shown to contain colloid. The influence of the colloids on the potential is also recorded. Bronze or yellow tints are often, but not invariably, present in copper containing colloids. The reduction in size of crystallites is attributed to adsorption, and the production of a laminated structure, which is often observed, to cataphoretic action.

Deposits from alkaline solutions of complex copper salts adhere firmly to the cathode, and are apparently structureless.

The hardness, determined by means of a sclerometer, is always the same on the surface in contact with the cathode, and is a maximum. The hardness on the outer surface diminishes with increasing crystal size. C. H. D.

The Kolbe Reaction with Sulphoacetic Acid. F. Fichter (*Zeitsch. Elektrochem.*, 1914, **20**, 471—473).—The electrolysis of methanedisulphonic acid, $CH_2(SO_2\cdot OH)_2$, with a current density of 1·2 amperes per sq. cm. causes a decomposition into sulphuric acid and carbon dioxide, with a current efficiency of 19·5%; ozone and persulphuric acid are also found in the products. Sulphoacetic acid, $SO_3H\cdot CH_2\cdot CO_2H$, yields the same products on electrolysis with a current density of 0·7 amp. per sq. cm. The current efficiency in this case is 44%. The acid salts of sulphoacetic acid behave in the same way as the free acid. In the case of normal potassium sulphoacetate electrolysis with a current density of 1—3 amperes per sq. cm. produces after a time an alkaline solution, which finally becomes faintly acid. A number of such experiments were carried out with both potassium and ammonium sulphoacetates; the liquid and the electrode gases have been analysed. All determinations lead to the view that the sulpho-acids behave in the same way as the carboxylic acids. The reaction in the present case is represented as follows:

(1) $H_2O + 2'O_3S\cdot CH_2\cdot CO_2' + 2F + 4K^{\cdot} = {}'O_3S\cdot CH_2\cdot CH_2\cdot SO_3' + 2KHCO_3 + 2K^{\cdot}$.

(2) $'O_3S\cdot CH_2\cdot CH_2\cdot SO_3' + 6O + 10F = 2SO_3'' + 2CO_2 + 2H_2O$.

The author is of the opinion that the Kolbe reaction is to be regarded as an oxidation process. The existence of ethanedisulphonic acid in the solution is confirmed by the isolation of the barium salt, $C_2H_4(SO_3)_2Ba,2H_2O$. J. F. S.

Application of the Theory of Allotropy to Electromotive Equilibria and Passivity of Metals. A. Smits (*Zeitsch. physikal. Chem.*, 1914, **88**, 743—757, and *Verst. K. Akad. Wet.*, 1912, **22**, 642).—A theoretical paper in which the theory of allotropy is applied to the electromotive equilibrium between a metal and an electrolyte. It is shown that a metal, which exists in allotropic forms, is made up of different kinds of molecules, and sends various

kinds of ions into the solution. The diagram representing this equilibrium is that of a pseudo-system, which in the present consideration has been regarded as a pseudo-binary system. The development of this idea in connexion with electrolysis leads to possible explanations of why in electrolysis it is, in many cases, the metastable and not the stable form of a metal which is deposited. It is also shown that with a definite current density the metal forming the anode becomes more electro-negative, whilst at the same time the cathode metal becomes less electro-negative, at least so far as their surface layers are concerned. The reason is offered for the fact that, when a metal is brought into contact with a solution of one of its salts, an increased rate of setting up the internal equilibrium of the metal is observed. The theory of allotropy leads to the view that when a metallic compound is reduced to metal at the lowest possible temperature, a product will be obtained which is far removed from its internal equilibrium, and which consequently will show an abnormal chemical activity. This state of things is probably the explanation of the remarkable behaviour of pyrophoric metals. J. F. S.

The Solution of Metals in Acids. A. Thiel (*Zeitsch. Elektrochem.*, 1914, **20**, 460—463).—Mainly polemical. The theory connecting over-voltage and passivity as put forward by Centnerszwer and Sachs (A., 1914, ii, 550) is criticised. It is shown that a connexion between over-voltage and solution tension has not been proved, and that the slowness of the solution of zinc in acid solutions has nothing whatever to do with passivity. The constant potential differences of the electrodes of local elements, in the process of solution, are not the cause, but rather the result, of the discharge of hydrogen ions. In any attempts to explain the phenomena which accompany the solution of zinc in acids, it is necessary to take into account the capillary relationships as well as the surface and over-voltage effects of metallic impurities. J. F. S.

Passivity. II. Influence of Substances of Different Chemical Nature on the Passivity of Iron. Fr. Flade and H. Koch (*Zeitsch. physikal. Chem.*, 1914, **88**, 307—320).—When an iron electrode is placed in a 0·1*N*-sulphuric acid solution and anodically polarised, a stationary condition sets in, in which a constant current passes, and the iron has a definite potential. If now the polarising potential is gradually changed, the electrode potential suddenly falls at a definite point, the value which it reaches representing a sharp transition from the active to the passive condition (Flade, A., 1911, ii, 461). The present paper deals with the influence of various substances on the stationary potential and the transition potential. It is shown that the strong surface-active substances amyl alcohol, *iso*butyl alcohol, and *iso*propyl alcohol are without influence, from which it follows that the existence of the passive layer is independent of the surface forces. The addition of weak acids, including butyric, valeric, heptoic, oxalic, malonic, succinic, benzoic, and phosphoric acids,

causes the transition potential to move to the more positive side, that is, there is less tendency for the iron to become active in the presence of these acids. The oxidising agents, chromic acid and permanganic acid, either entirely prevent the iron from becoming active or by changing the transition potential render it less likely to become active. The reducing agents sulphurous acid and phosphorous acid tend to convert passive iron into the active form, whereas hydroxylamine, hydrogen sulphide, and hydrogen cyanide are without influence. Hydrogen peroxide increases the current strength at the stationary point, and thus acts as a reducing agent. This effect is at first strong, but decreases with time. The transition potential is moved by hydrogen peroxide to the more positive side, and in this action it behaves as an oxidising agent. The influence of halogen ions, added in the form of hydrochloric, hydrobromic, and hydriodic acids, is to cause passive iron to become active under conditions which normally would ensure its remaining passive. The change from passive iron to active iron in these cases is preceded by an induction period. J. F. S.

Passivity. III. The Hydrogen Hypothesis. Fr. Flade (*Zeitsch. physikal. Chem.*, 1914, **88**, 569—607. Compare A., 1911, ii, 461, and preceding abstract).—The present paper opens with a long theoretical introduction, which purports to be an attempt to decide between the oxygen hypothesis and the hydrogen hypothesis of passivity. The major portion of the discussion is a criticism of Rathert's paper, which favours the hydrogen hypothesis (A., 1914, ii, 242). The author states that of Rathert's experiments which are supposed to be decisive, every one is open to objection, and none of them point to the correctness or otherwise of either theory. The objections offered by Rathert to the methods adopted by the author for the determination of passivity or activity in iron (*loc. cit.*) do not apply to the method at all. The view that iron which has been ignited in a vacuum still contains hydrogen is extremely unlikely, and the statement, that the activity of iron is brought about by small quantities of hydrogen, is without foundation. A number of experiments are then described on the passivity of chromium, from which it is shown that it is possible for passive chromium to give off hydrogen in acid without becoming active, so that the hydrogen hypothesis in this case cannot be correct.
J. F. S.

The Influence of Molecular Constitution and Temperature on Magnetic Susceptibility. III. The Molecular Field in Diamagnetic Substances. A. E. Oxley (*Phil. Trans.*, 1915, [*A*], **215**, 79—103).—A paper, mainly theoretical, in which the author shows how observations relating to the change in the diamagnetic susceptibility on the crystallisation of a substance may afford information concerning the inner structure of crystals and the intensity of the interacting molecular forces.

Further experiments on the change of the diamagnetic susceptibility of organic substances in passing from the liquid to the

crystalline state confirm the previous observation that aromatic substances show an appreciable change, whilst aliphatic compounds exhibit little or no alteration in susceptibility on solidification.

On comparing the percentage changes of susceptibility on crystallisation with the values obtained for the magnetic double refraction by Cotton and Mouton (A., 1907, ii, 727; 1908, ii, 2, 745, 757; 1909, ii, 773; 1910, ii, 368), a close parallelism between the two series of numbers is found, and this is considered to indicate that the two effects are connected. Mono-substituted benzene derivatives show changes of diamagnetic susceptibility on crystallisation, which are of the same order of magnitude. This is also true of the values of the magnetic double refraction. The nitro-group forms an exception in both cases, in that its influence is abnormally large. The fact that *cyclo*hexane affords a zero value for both effects would seem to show that these depend on the degree of unsaturation of the substance. H. M. D.

γ-Ratio of the Two Principal Specific Heats of Gaseous Mixtures. Applications. A. Leduc (*Compt. rend.*, 1915, **160**, 338—341).—A mathematical treatment of the problem (compare A., 1898, ii, 326). W. G.

The Ratio $k=C_p/C_v$ of the Specific Heats of Gases at Constant Pressure and Constant Volume for Different Pressures. K. Schöler (*Ann. Physik*, 1914, [iv], **45**, 913—928).—The influence of pressure on the specific heat ratio has been examined in a series of experiments with air, carbon dioxide, sulphur dioxide, ammonia, and ethylene at pressures varying from 0·33 to 4 atmospheres. The ratio was obtained from measurements of the velocity of sound in the gases by Behn and Geiger's modification (*Ber. Deut. physikal. Ges.*, 1907, 657) of the Kundt method.

Values of the ratio are recorded, which are derived (1) on the assumption that the gases obey the simple gas laws, (2) by taking into account the deviations from the gas laws. The second series of values increases in all cases with increasing pressure, and the increment increases with the magnitude of the deviation of the compressibility from that required by Boyle's law. This is seen from the following values: air, 1·404 at 0·5, 1·411 at 3·5 atm.; carbon dioxide, 1·288 at 0·5, 1·307 at $3\frac{2}{3}$ atm.; sulphur dioxide, 1·273 at 0·5, 1·347 at 2·5 atm.; ammonia, 1·297 at 0·5, 1·410 at 3·5 atm.; ethylene, 1·275 at 0·5, 1·334 at $3\frac{2}{3}$ atm. H. M. D.

Measurement of Specific Heats and Molecular Weight Determination. Rudolf Ewald (*Ann. Physik*, 1914, [iv], **44**, 1213—1237).—The calorimeter described by Nernst, Lindemann, and Koref (A., 1910, ii, 263) has been used in the measurement of the mean specific heats of elements and compounds over the temperature intervals 55° and 0°, 0° and −78°, −78° and −190°. The results obtained with certain ammonium salts (chloride, iodide, and sulphate) are anomalous, in that the specific heat between 0° and −78° is greater than that between 55° and 0°. Dilatometer experi-

ments have shown that the change in volume is quite normal over this range of temperature, and in consequence the anomaly in the specific heat cannot be attributed to the existence of a transition point.

The specific heat-temperature curves are discussed in reference to the Nernst-Lindemann and Debye formulæ, and from the form of the experimental curves the conclusion is drawn that cadmium, tin, thallium, magnesium, and iron are probably monatomic, whilst phosphorus, arsenic, bismuth, and antimony are polyatomic. In regard to the deduction of molecular weights from the temperature variation of the specific heat, it is pointed out that this method affords greater certainty in the case of elements which consist of polyatomic molecules. H. M. D.

Regularities Connected with the Internal Work of Expansion on Warming Liquids and the Relationship of the Specific Heats of Liquids. F. A. Schulze (*Zeitsch. physikal. Chem.* 1914, **88**, 490—505).—A theoretical paper in which it is shown that the product of the molecular weight of most normal liquids and the difference of the specific heats, that is, $M(C_p - C_v)$, is practically a constant at constant temperature (compare Tyrer, A., 1914, ii, 431). Associated liquids and some non-associated liquids, however, do not show this regularity. The expression $M(C_p - C_v) = K$ is developed mathematically, and in this connexion it is shown that the expression can only be true for corresponding reduced temperatures and pressures and for non-associated liquids. The value C_p/C_v is considerably greater than unity for many liquids, and the values of C_p/C_v calculated from thermodynamical data and those obtained from the velocity of sound are in close agreement with one another. J. F. S.

Specific Heat. II. Alkali Haloids. J. N. Brönsted (*Zeitsch. Elektrochem.*, 1914, **20**, 554—556).—The specific heats and molecular heats of seventeen alkali haloids have been determined at 10°. The dry salts were cooled to 0°, and transferred to a gold-plated silver calorimeter at 19·6°. The temperature change was measured by means of a fine platinum resistance thermometer. The following values of the specific heat were obtained: LiF, 0·3725; NaF, 0·2610; NaCl, 0·2027; NaBr, 0·1176; NaI, 0·0821; KF, 0·1997; KCl, 0·1614; KBr, 0·1031; KI, 0·0741; RbF, 0·1153; RbCl, 0·1013; RbBr, 0·0743; RbI, 0·0581; CsF, 0·0796; CsCl, 0·0746; CsBr, 0·0582; and CsI, 0·0477. It is shown that with the exception of cæsium chloride the molecular heat increases with increasing atomic weight of the metal, and also with increasing atomic weight of the halogen. Curves of the relationship of the molecular heat with the molecular weight are given (compare A., 1912, ii, 897). J. F. S.

Chemical Affinity. IX. Transition of Tin Allotropes. J. N. Bronsted (*Zeitsch. physikal. Chem.*, 1914, **88**, 479—489).—The heat of transition of grey tin into white tin and the specific heat of both varieties of tin have been directly measured. The heat evolved

by the change $Sn_{white} \rightleftharpoons Sn_{grey}$ at $T=273°$ has been found to be 532 cal. per gram atom. The specific heat of both varieties was measured between $T=80°$ and $T=273°$, and the values found agree exactly with those previously deduced from measurements at $T=283°$ (A., 1913, ii, 295). When it is assumed that the Debye formula for specific heat is true between 0° and 60°, and that the value of Θ, a characteristic constant, is 198 for white tin and 253 for grey tin, then it is shown that the course of the curves representing the relationship between temperature and heat of transition (**U**-curve) and between temperature and transition affinity (**A**-curve), is in strict accord with the Nernst heat theorem.

J. F. S.

Measurement of the Freezing-point Depression of Dilute Solutions. Leason H. Adams (*J. Amer. Chem. Soc.*, 1915, **37**, 481—496).—A method is described for determining the depression of the f. p. of dilute solutions by means of a 50-junction copper-constantan thermo-element and a sensitive potentiometer system. In order to secure a condition of stationary equilibrium, the solution is mixed thoroughly with a large quantity of ice in a vacuum-jacketed vessel surrounded by melting ice. The concentration of the equilibrium solution is determined by a zero method, using an interferometer as a means of comparison.

The method has been tested by measurements of solutions of mannitol, potassium nitrate, and potassium chloride of concentrations ranging from 0·004*M* to 0·1*M*, and the results show that it has an accuracy of ±0·0001°. E. G.

Variation of the Cryoscopic Constant with the Molecular Weight of the Solvent. J. de Guzmán Carrancio (*Anal. Fis. Quim.*, 1915, **13**, 89—98).—The author gives a series of tables showing the value of the cryoscopic constant for a number of solvents. His results indicate that increase in molecular weight for compounds of the same series is attended by an increase in the cryoscopic constant. This constant also appears to be a periodic function of the elements, since it increases with augmentation of the atomic weight for the elements of the same group. A. J. W.

Chloral Hydrate and Bromal Hydrate as Cryoscopic and Ebullioscopic Solvents. Ernst Beckmann and Maria Maxim (*Ber.*, 1914, **47**, 2875—2880).—An investigation of the applicability of chloral and bromal hydrates as solvents for molecular-weight determination. The proximity of the transition point of two crystalline forms to the freezing point of chloral hydrate makes it unsuitable as a cryoscopic solvent, but it can be employed for ebullioscopy. Bromal hydrate is useful as a cryoscopic solvent, but decomposes too readily to be used as an ebullioscopic solvent. For chloral hydrate the differences of temperature are small, and there is a tendency to fission of water and hydrochloric acid, so that the results should be accepted with reserve.

Bromal hydrate must be dry, and care must be taken to main-

tain uniform experimental conditions, such as external temperature, velocity of crystallisation, and mode of operating. This solvent has a greater tendency to decompose than chloral hydrate.

The ebullioscopic constant (K) of chloral hydrate is 22·5, and the cryoscopic constant (K) of bromal hydrate is 110·4. The corresponding latent heats (w) are 121·4 and 19·31. A. J. W.

Ebullioscopic Behaviour of Solvents at Different Pressures. II. Acetic Anhydride and Acetic Acid. Ernst Beckmann and Otto Liesche [with Julius von Bosse] (*Zeitsch. physikal. Chem.*, 1914, **88**, 419—427).—The ebullioscopic constant of acetic anhydride has been determined at pressures from 1171 mm. to 203 mm., using benzil as dissolved substance. Similar determinations have been made for acetic acid at pressures from 1126 mm. to 197 mm., using diphenylamine as dissolved substance. The results of these determinations are compared with other data, particularly the degree of association, of these solvents. Acetic anhydride shows a slight association, which is in accord with the slight divergence from the normal value as shown by the Trouton rule. On the other hand, the ebullioscopic constant calculated from the Walden formula gives a value much in excess of that determined experimentally. The constant for atmospheric pressure is 35·3, and from this the latent heat of vaporisation is calculated to 94·3. Acetic acid, despite its abnormal character, gives a constant which, with the exception of that from the Walden formula, agrees well with the calculated values. This is explained by the fact that the association of acetic acid does not change much in the passage from liquid to vapour. The molecular weight of acetic acid in the vaporous condition is 102, thus showing an association factor of 1·7, and the value is not much changed by a change of pressure. The ebullioscopic constant is 30·7, giving a latent heat of vaporisation of 99·1. J. F. S.

An Apparatus for Fractional Distillation in a Vacuum. A. Heiduschka and E. Rheinberger (*J. pr. Chem.*, 1914, [ii], **90**, 354—356).—The apparatus, which permits of continuous fractional distillation at pressures of less than 1/1000 mm., consists of the following parts, connected together with glass tubes, the junctions, where not fused together, being made air-tight by mercury seals: A distilling flask with a side-inlet tube which can be sealed off, and surmounted by a column with pear-shaped bulbs, in the top of which is fixed the thermometer in a mercury seal. An Erlenmeyer flask into the base of which are sealed small glass bulbs with long necks to collect the distillate. A cup is fused round the neck, and the flask is connected with the side-tube of the column in such a way that it can be rotated so as to bring the collecting bulbs in turn under the exit. The junction between the tube and the flask is made air-tight by filling the cup with mercury. Fused into the side of the Erlenmeyer flask is a tube leading in turn to a flask containing wood charcoal, a manometer, a cathode tube, and two glass cocks. In use, after the substance has been placed in the

distilling flask and the inlet sealed off, the apparatus is exhausted by a water-pump connected to one of the cocks. Carbon dioxide is then let in through the other cock, and the operation repeated two or three times. The water-pump is then cut off, and the exhaustion continued with a mercury pump attached to the second cock. The cathode tube is used to ascertain the height of the vacuum attained. When the distillation is completed, the collecting bulbs containing the individual fractions are sealed off whilst the vacuum is maintained. To render the two glass taps in the apparatus perfectly air-tight a mixture of lanoline and wax is recommended, in proportions suitable to the prevailing temperature. G. F. M.

Laboratory Apparatus for Fractional Distillation. E. Chenard (*Bull. Soc. chim.*, 1915, [iv], **17**, 38—41).—A reply to Vigreux (A., 1914, ii, 711). W. G.

The van der Waals' Formula (and the Latent Heat of Vaporisation). T. Carlton Sutton (*Phil. Mag.*, 1915, [vi], **29**, 593—599).—In a recent paper Applebey and Chapman (T., 1914, **105**, 734) have deduced a formula for the latent heat of vaporisation which is shown to yield results in good agreement with the values obtained from Young's vapour-pressure measurements. The author points out that the Mills-Young values are also to be regarded as calculated values, and that these are obtained by a process very similar to that employed by Applebey and Chapman. The chief difference lies in the fact that Mills makes use of Biot's formula, $\log p = A + B\alpha^t + C\beta^t$, to express the relation between the vapour pressure p and the temperature t, whereas Applebey and Chapman use a form of van der Waals' equation, in which b is dependent on the temperature. Since b varies uniformly with the temperature, this equation may be written in the form:

$$(p + a/v^2)(v - b - \nu\delta t) = Rt,$$

where $\nu = db/dt = \text{constant}$. The two formulæ for the latent heat of vaporisation are thus derived from relations which approximately represent the same experimental results. H. M. D.

The Boiling Points and Critical Temperatures of Homologous Compounds. Allan Ferguson (*Phil. Mag.*, 1915, [vi], **29**, 599—608).—An empirical formula connecting the boiling points and the molecular weights of the normal paraffins is put forward. This may be written in the form $\log\theta = k(\log M)^s$, in which θ is the absolute boiling point, M the molecular weight, and $k = 1{\cdot}929$ and $s = 0{\cdot}4134$ are constants. The average difference between the calculated and observed temperatures for paraffins containing four to seventeen carbon atoms is equal to 0·64°.

The ratio of the critical temperature to the boiling point varies in a regular manner in the normal paraffins, and it is shown that this ratio (θ_c/θ) is connected with the number of carbon atoms in the molecule (n) by the relation $\theta_c/\theta = h/n^g$, in

which $h=1\cdot841$ and $g=0\cdot120$. The average difference between the calculated and observed values of the ratio θ_c/θ over the range $n=2$ to $n=10$ amounts to 0·33%.

By eliminating θ from the equation $\theta_c=h\theta/n^g$ and any one of the several equations connecting the boiling point with the molecular weight, equations are obtained which express the relation between the critical temperature and the molecular weight. Using for this purpose the equation $\log\theta=k(\log M)^s$, the derived equation assumes the form $\log\theta_c=\log h+k(\log M)^s-g\log n$, in which k, s, g, and h are constants having the values recorded above.

Empirical formulæ expressing the influence of substitution in the normal paraffins are also discussed. It is shown that the boiling points of the primary alkyl bromides, θ_B, are connected with those of the corresponding paraffins, θ_P, by the equation:

$$\theta_B-\theta_P=187\cdot5/n^{0\cdot436}.$$

Average error over the range $n=3$ to $n=8$ is 0·73°. A similar formula for the primary alcohols $\theta_A-\theta_P=331\cdot1/n^{0\cdot7456}$ gives the boiling points of the alcohols between $n=3$ and $n=10$, with an average error of 2·04°. H. M. D.

The Temperature Relationship of Some Physical Properties of Water in its Various States of Aggregation. Ivar W. Cederberg (*Physikal. Zeitsch.*, 1914, **15**, 824—831).—A theoretical paper in which temperature relationships of many physical properties of water are considered. The formula:

$$\log p=-M\lambda_0/RT+1\cdot75\log T-M\epsilon/R\,.\,T+C,$$

is developed from the Clausius-Clapeyron formula. In this expression M is the logarithmic modulus, λ_0 the molecular heat of vaporisation at the absolute zero, ϵ an empirical constant, and C the integration constant. This constant is termed by Nernst the "chemical constant." The paper deduces a method of calculating the value of C, and this is done for a number of substances. From the results it is shown that with the exception of helium and hydrogen, $C=\log\pi_0+1\cdot2$, where π_0 is the critical pressure. The vapour pressure of ice and liquid water can be expressed by the formula $\log\pi_0/p=\alpha\,.\,\beta.^{(T/\theta-\gamma)^2}.(\theta_0/T-1)$ to the very lowest temperatures. By combining this formula with the Clapeyron formula the heat of vaporisation of water and the heat of sublimation of ice are accurately calculated. The difference between the molecular heat of a saturated vapour at constant pressure and that of the condensed product is calculated. It is shown that this quantity $(Cp-c)$ is very little influenced by temperature, and over the range 0—50° has a value −9·806, the value at 0° being −9·8. If the molecular heat of liquid water at 0° is assumed to be 18, then $Cp=8\cdot2$, which is very near to that required by the kinetic theory, $4R=7\cdot94$. J. F. S.

Calculation of the Heat of Vaporisation from the Berthelot Condition Diagram. J. Riddick Partington (*Zeitsch. physikal. Chem.*, 1914, **88**, 297—306).—A theoretical paper. The latent heat of vaporisation of a number of liquids is calculated by means of the

formula $\lambda = 27/64 \cdot R^2(T_k^2/p_k v_1) + RT_1$, due to Bakker, and by the formula $\lambda = 27/64 \cdot R^2 \cdot (T_k^3/p_k v_1 T_1) + RT_1$, deduced by the author. In the equations λ is the molecular latent heat, v_1 the volume of the liquid, T_k and p_k the critical temperature and pressure respectively, T_1 the boiling point, and R the gas-constant. It is shown that with the exception of oxygen and nitrogen, the values calculated by the second formula agree much more nearly with the experimentally determined values than do those calculated by the Bakker formula. Strongly associated liquids give quite different values in both cases. It is shown that the Trouton rule is not in accord with the Berthelot equation. The theory of the heat of vaporisation of binary mixtures is discussed, and formulæ are developed for calculating this quantity. J. F. S.

Gaseous (Inter)-metallic Compounds. H. VON WARTENBERG (*Zeitsch. Elektrochem.*, 1914, **20**, 443—449).—The probability of the existence of gaseous intermetallic compounds is discussed in connexion with the Nernst heat theorem, and it is shown that such compounds can, in general, only exist at low temperatures and small pressures. The two compounds $MgZn_2$ and Na_3Hg are examined experimentally. The former compound is shown to have a heat of formation of 1314 ± 180 cal. from measurements of the heat of solution of Mg, Zn, and $MgZn_2$, and the reaction $Mg_{gas} + 2Zn_{gas} = MgZn_{2gas}$ a value of $+59000$ cal. The compound Zn_2Mg distils undecomposed at 600°, but is completely dissociated at 1300°. The vapour pressure of Na and Na_3Hg has been determined at 444°, and the following values obtained: 6·92 mm. Hg ± 3% for Na_3Hg and 0·56 mm. Hg ± 6% for sodium. Attempts to determine the vapour density of Na_3Hg failed entirely, but from the heat of formation, which was found to be 13,000 cal. ± 10% for the solid compound, and distillation experiments, it is shown that Na_3Hg is stable in the vapour phase between 380° and 444°. J. F. S.

Investigations on Ammonia. I. General Considerations. F. HABER (*Zeitsch. Elektrochem.*, 1914, **20**, 597—604).—A résumé of the results of a number of researches on ammonia to be published shortly. The equilibrium constant for the formation of ammonia from nitrogen and hydrogen in the presence of osmium as catalyst at temperatures from 974° to 561° is given by the expression:

$$\log K_p = 9591/4{\cdot}571T - 4{\cdot}98/1{\cdot}985 \log(T) - 0{\cdot}00046/4{\cdot}571(T) + 0{\cdot}85 \times 10^{-6}/4{\cdot}571(T^2) + 2{\cdot}10.$$

Using uranium carbide as catalyst this expression can also be used for temperatures up to 1100° and below 600°. The specific heat of ammonia gas is given by the expression:

$$C_p = 8{\cdot}62 + 0{\cdot}0035t + 5{\cdot}1 \times 10^{-6}t^2,$$

and the heat of formation $= 10950 + 4{\cdot}85t - 0{\cdot}00093t^2 - 1{\cdot}7 \times 10^{-6}t^3$ cal. The results of other experiments with molybdenum and tungsten as catalysts are also given. J. F. S.

Free Energy of Some Carbon Compounds. GILBERT N. LEWIS and MERLE RANDALL (*J. Amer. Chem. Soc.*, 1915, **37**. 458—470).—In

continuation of the work on free energy (A., 1913, ii, 112; 1914, ii, 802, 840; this vol., ii, 12), the authors have calculated the free energy of carbon and some of its compounds from existing data, and have obtained the following values (in calories) for the free energy of formation (Δ F° 298). Diamond, 520; carbon monoxide (gas), −32,560; carbon dioxide (gas), −94,360; carbonic acid (in aqueous solution), −148,970; the ion, HCO_3', −140,140; the ion, CO_3'', −126,130; methane, −12,800; carbonyl chloride, −45,380.

E. G.

Heats of Formation of Acraldehyde and Metacraldehyde. E. VOISENET (*Bull. Soc. chim.*, 1915, [iv], **17**, 34—37).—The author has determined the heats of combustion of acraldehyde and metacraldehyde by burning them in a Berthelot bomb calorimeter. Weighed quantities of the aldehydes were sealed in glass bulbs, these being burst in the calorimeter by a small amount of combustible material, the calorific value of which was exactly known. From the results of these experiments the heats of formation of the two aldehydes were calculated, the values obtained being, for acraldehyde, 27·48 Cal., and for metacraldehyde, 92·65 Cal. The reaction:

$$OH\cdot C_3H_2\cdot CH(OH)\cdot CH_2\cdot OH = 2H_2O + CH_2{:}CH\cdot CHO$$

is therefore slightly exothermic, giving 3·78 Cal. W. G.

Theoretical Treatment of the Phenomena in Dilute Gases. M. VON SMOLUCHOWSKI (*Ann. Physik*, 1914, [iv], **45**, 623—624).—A correction of certain misconceptions in Baule's paper (A., 1914, ii, 425) dealing with the phenomena exhibited by gases at very low pressures. The calculations made by Baule are considered to lend support to the author's views. H. M. D.

The Heat Development in the Swelling of Colloids. ERNST ROSENBOHM (*Koll. Chem. Beihefte*, 1914, **6**, 177—200).—The heat changes attending the absorption of water by various colloids have been measured by means of a Bunsen ice calorimeter. In the case of gelatin, the influence of dissolved salts and other substances on the thermal effect was also examined.

Experiments with carefully dried substances in excess of water gave the following values for the heat development per gram: gelatin, 36·0 cal.; agar-agar, 35·5 cal.; filter-paper, 9·6 cal.; pure cellulose, 12·9 cal.; cotton-wool, 20·8 cal.; hair, 17·0 cal. From experiments with gelatin containing variable amounts of absorbed water, it is found that the heat change is practically confined to the initial stage of the swelling. When the gelatin has taken up about 50% of water, the further absorption is not accompanied by any appreciable heat effect.

Experiments with air-dried gelatin and aqueous solutions of salts show that the thermal effect depends on the nature of the dissolved substance and on its concentration. In the case of sodium and potassium chloride solutions, the thermal effect increases linearly with the concentration. Lithium chloride, potassium nitrate, and

ammonium nitrate show a maximum heat development at a particular concentration. Potassium iodide shows a maximum at about $1N$, and this is followed by a minimum at about $3N$. Potassium bromide behaves similarly.

In sodium sulphate, potassium sulphate, and potassium hydrogen sulphate solutions, the heat effect increases with the concentration of the solution, but the relationship is not linear as for the chlorides. Magnesium sulphate shows a maximum at about 1 molar concentration. In potassium chromate and chrome alum solutions the heat of swelling is less than in water. This behaviour of the chromium compounds is doubtless connected with the chemical action of these substances on the gelatin.

In sucrose and glycerol solutions the heat of swelling is also less than in water, and diminishes approximately linearly as the concentration increases. H. M. D.

Heat Effect of Solution. M. Levalt-Ezerski (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 177—185).—Further development of the considerations of the author's previous paper (A., 1912, ii, 737) leads to the conclusion that, when, with rise of temperature, the coefficient of contraction increases, solution takes place with generation of heat, whilst, when it diminishes, heat is absorbed on solution. Calculation by means of the data given by various authorities for solutions of various concentrations of K_2SO_4, $MgCl_2,6H_2O$, NH_4Cl, $CaCl_2,6H_2O$, $Pb(NO_3)_2$, $NaNO_3$, $ZnSO_4,7H_2O$, and H_2SO_4 shows that the above rule is obeyed in each of these cases.

Further calculations have been made in the following manner. The magnitudes of the coefficient of contraction corresponding with dilution of an n% solution to (1) m%, and (2) l% (where l is less than m) at $t°$ are calculated, and are termed respectively k_1 and k_2; similar calculations are then made for a higher temperature, the concentrations of the solutions being the same as before. These calculations have been made for lithium, sodium, potassium, and magnesium chlorides, potassium bromide, sodium iodide, sodium, potassium, and ammonium nitrates, sodium and potassium carbonates and sucrose. In all these instances it is found that, if rise of temperature is accompanied by algebraic increase of the difference, $k_1 - k_2$, the compound dissolves with development of heat, and inversely. With aqueous solutions of ethyl alcohol, not only is this rule obeyed at all concentrations, but the maximum heat effect accompanying mixing of the components corresponds with the maximum thermal change of the coefficient of contraction.

Thomsen ("Thermochemistry," Vol. I.) states that: "Independently of the sign of the heat effect observed on diluting an aqueous solution, the change of the heat effect with rise of temperature is always positive." The results of the author's calculations show that the coefficient of contraction on dilution always changes in the negative direction with rise of temperature. T. H. P.

Cohesion and Atomic Volume. P. Ludwik (*Zeitsch. physikal. Chem.*, 1914, **88**, 632—637).—A theoretical paper in which the

expression $\sigma_B = kn(T_s - T)$ is put forward as a relationship between the cohesion and the atomic volume. In the expression, σ_B represents the resistance of a metal or other substance to a pull (zugfestigkeit), k is a constant, n the reciprocal of the atomic volume, and $T_s - T$ is the difference between the temperature of the melting point and the experimental temperature, both in degrees absolute. The value of σ_B is at a maximum at $T=0$, and then has the value knT_s, and this is approximately proportional to $c/\alpha.\gamma$, where c is the specific heat, α the coefficient of expansion at the same temperature as c is determined, and γ the specific gravity (A., 1914, ii, 531). A series of values of σ_B calculated for $T=290°$ by the formula are compared with the experimentally determined values, and a moderate agreement is obtained.

J. F. S.

Compressibilities of Mercury, Copper, Lead, Molybdenum, Tantalum, Tungsten, and Silver Bromide. Theodore W. Richards and Edward P. Bartlett (*J. Amer. Chem. Soc.*, 1915, **37**, 470—481).—An account is given of the determination at 20° of the compressibilities of certain substances between 100 and 500 megabars by the method used in earlier work (A., 1904, ii, 384; 1907, ii, 858; 1909, ii, 214; 1912, ii, 896). In the most accurate experiments the piezometer was made of soft steel instead of glass, in order to obviate the hysteresis of glass under high pressure. The results have shown, however, that this difficulty had already been overcome by the method of manipulation, and that the earlier results are actually quite as satisfactory as was supposed. The differences in the final values of the compressibilities are due chiefly to a change in the assumed compressibility of mercury which has been referred to a new absolute value for iron ($0{\cdot}61 \times 10^{-6}$).

The compressibilities found expressed in the megabar standard $\times 10^6$ (A., 1904, ii, 385), are as follows: copper, 0·76; lead, 2·35; mercury, 3·96; molybdenum, 0·47; tantalum, 0·54; tungsten, 0·28; silver bromide, 2·70. The compressibilities of tantalum and tungsten have not been determined previously; the values found for copper, iron, and lead agree well with those obtained by Grüneisen (A., 1911, ii, 188). It is pointed out that tungsten seems to have the smallest compressibility of any of the substances hitherto studied.

E. G.

The Mechanical Anisotropy of Metals and Alloys with Large Grains, and the Ball Test. A. Portevin (*Compt. rend.*, 1915, **160**, 344—346. Compare A., 1913, ii, 479, 598).—The author has examined the shape of the impress formed by the dropping ball in the case of various alloys possessing a coarse-grain structure. Examples have been taken where only one grain has been struck under various conditions, and where several grains, similarly orientated, have been struck. The results show that the impress on each grain is far from being circular on account of the mechanical anisotropy of the grain. The results explain why the impressions obtained in the case of metals and alloys with large grains, orien-

tated in a manner such that several grains are deformed, are extremely irregular, and do not give any exact measurements.

W. G.

Viscosity of Liquid Mixtures. II. A. N. Sachanov and N. A. Rjachovski (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 113—133. Compare A., 1914, ii, 343).—It has been shown that the viscosity of a mixture of two liquids is represented by the equation:

$$\eta=\eta_1(1-x)^2+\eta_2x^2+n\sqrt{\eta_1\eta_2}\,.x(1-x) \quad . \quad . \quad (1),$$

where x is the proportion of the second component per mol. of the mixture, and n is a constant. According to the law of additivity, this expression should be:

$$H=\eta_1(1-x)+\eta_2x \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

From these relations it follows that:

$$\eta=H-kx(1-x) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3),$$

where

$$k=\eta_1+\eta_2-n\sqrt{\eta_1\eta_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

The constant n will have the value 2 in the simplest case, but will in general be somewhat less than 2, so that k will always be positive and the viscosity of the mixture always less than the calculated additive value. Equation (4) gives:

$$dk/d\eta_1=1-n\sqrt{\eta_1/\eta_2}/2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5),$$

and from this, if η_1 be taken to be greater than η_2, it follows that the greater the difference between the viscosities of the two components the greater will be k and the greater the deviation of the viscosity curve from the straight line representing additivity. Of all the binary mixtures of non-interacting components which have been previously examined, benzene–tetrachloroethane at 0° is the only one giving a slightly convex viscosity curve, that is, a negative value of k. This exceptional result appears to be due to the anomalous behaviour of benzene at low temperatures (compare Batschinski, A., 1913, ii, 928), and this conclusion seems to be confirmed by Linebarger's observation (A., 1896, ii, 408) that at 25° the same mixtures yield a concave viscosity curve, and, consequently, a positive value for k.

Equations (1) and (3) apply more generally than to the viscosity alone, many other properties of liquid mixtures obeying approximately the same relations. Thus, Herzen (A., 1903, ii, 132) found that the surface tension of liquid mixtures is not a linear function of the composition, the form of the curve depending on the van der Waals' equation for the magnitude a, and Stefan's relation between a and the surface tension. Equation (3) is analogous to that expressing the volumes of liquid mixtures (compare von Biron, A., 1910, ii, 393), but in the latter case k may be either positive or negative, corresponding with contraction or expansion on mixing.

Equation (1) or (3) is applicable when the components of the mixture exhibit no chemical interaction or depolymerisation, the curve taking a higher course if such an effect is present. In some instances, chemical interaction of the two components results in the formation of extremely viscous, non-crystallising compounds,

the interaction proceeding to an end. In such cases the viscosity curve consists of a steep ascending branch and a steep descending one, the point of intersection corresponding with the compound formed. The viscosities of these compounds may be hundreds of times as great as those of the constituents. Of this type are the systems investigated by Kurnakov and his collaborators (A., 1913, ii, 190, 388). More commonly, however, the reaction between the components is restricted, and proceeds only as far as a stage of equilibrium between the compound and its constituents. The corresponding viscosity curves may either show a maximum, or be convex with no maximum, or be rectilinear or have the ordinary concave, hyperbolic form obtained with non-interacting components.

With similar intensity of interaction, the influence of complex-formation on the form of the curve will increase as the difference between the viscosities of the components diminishes, and only when this difference is small is the viscosity curve capable of giving an indication of a slight chemical interaction.

These considerations are entirely borne out by the authors' measurements at 0° and at 25° of the viscosities of binary mixtures of ketones and simple ethers with various halogenated hydrocarbons.

The first group of systems investigated comprises (1) those containing relatively slightly halogenated derivatives, such as ethyl bromide, chlorobenzene, dichloroethane, etc., and (2) those formed by highly halogenated compounds, such as carbon tetrachloride or tetrachloroethane. These systems exhibit no sign, in the form of development of heat or marked change in volume, of chemical interaction, and their viscosity curves are typical examples of the normal, more or less concave form. The other group consists of systems composed of such halogenated derivatives as dichloromethane, chloroform, tetra- or penta-chloroethane, and of the same ketones and esters as before, namely, acetone, ether, acetophenone, phenetole, and diphenyl ether. These systems are characterised by chemical interaction between the components, such interaction being less marked with the aromatic ketones and ethers than with those of the aliphatic series. In spite of this interaction, the viscosity curves for acetone–dichloromethane, acetone–tetrachloroethane, acetone–pentachloroethane, ether–tetrachloroethane, ether–pentachloroethane, and phenetole–chloroform are in good agreement with equation (3), the deviations never exceeding 1—3%. With acetophenone–chloroform and diphenyl ether–pentachloroethane, the curves are rectilinear, so that the value of k in equation (3) is zero. This accordance with equation (3) is shown to be due to the fact that the complex formed by the two components contains, in all these cases, one molecule of each component (compare Dolezalek and Schulze A., 1913, ii, 482). To the systems, acetone–chloroform, ether–chloroform, acetophenone–tetrachloroethane, and acetophenone–pentachloroethane, equation (3) is inapplicable.

The structures usually accepted for these double compounds of ethers or ketones with halogenated derivatives represent the oxygen as quadrivalent, and, according to these formulæ, the chloroform

or other halogenated compound plays the part of a very feeble acid, since the oxonium linking possesses a clearly marked basic character. From the authors' results it appears that only compounds containing a considerable proportion of the negative halogen atom, such as chloroform, tetra- and penta-chloroethanes, and, to a less extent, dichloromethane, exhibit appreciable acidic properties, and are able to react with ethers and ketones. Such acidic properties and ability to react with ethers and ketones are not shown by carbon tetrachloride and hexachloroethane, which contain no hydrogen atom.

In view of Bingham's assertion (A., 1906, ii, 218) that the fluidity of binary mixtures is a linear function of the composition (see also A., 1914, ii, 343), the authors have calculated the values of the fluidities for such mixtures as show absence of interaction between the components. Marked deviations from the linear relation are found in all these cases, irrespective of whether the compositions of the mixtures are expressed as percentages by weight or volume or as molecular percentages; the extent of the deviation increases with the difference between the fluidities of the components.

T. H. P.

Viscosity of the System Aniline–Allylthiocarbimide. N. KURNAKOV and J. KWJAT (*Zeitsch. physikal. Chem.*, 1914, **88**. 401—413).—Since aniline and allylthiocarbimide readily react to form phenylallylthiocarbamide, the above-mentioned system was examined by determining the viscosity of mixtures of phenylallylthiocarbamide and aniline or allylthiocarbimide. The measurements were carried out at 100° and 125° by the method previously described (Kurnakov and Schemtschuschny, *Zeitsch. physikal. Chem.*, 1913, **83**, 488; Kurnakov and Jefremov, *ibid.*, 1913, **85**, 401). It is shown that the viscosity curve of the system belongs to the "rational" type, and possesses an inflexion point for the relationship 1 : 1 of the components. This point, which corresponds with phenylallylthiocarbamide, is also obtained in the fusion curve diagram. The ternary system, aniline–allylthiocarbimide–toluene, is also examined in the same way, and it is shown that the position of the inflection point is not changed by the presence of the third substance. In the latter case the viscosity measurements were made at 85° and 100°; the temperature-coefficient of the viscosity is calculated in all cases, and three dimensional diagrams are given.

J. F. S.

The Kinetics of Sorption. A. DIETL (*Koll. Chem. Beihefte*, 1914, **6**, 127—146).—The rate at which acids are absorbed from aqueous solution by wool has been investigated by experiments at 20° with hydrochloric, hydrobromic, nitric, sulphuric, phosphoric, formic, acetic, propionic, butyric, oxalic, and succinic acids. If a denotes the equilibrium concentration of the acid in the wool, and x the concentration after an interval t, and it is assumed that the sorption velocity at any moment is proportional to the difference $a-x$ as represented by the equation $dx/dt=k(a-x)$, values are obtained for the coefficient k which decrease as the sorption pro-

ceeds. On the further assumption that the process is autocatalytically retarded, the sorption velocity at any moment is represented by the equation $dx/dt=(k_1-k_2x)(a-x)$, and the observations are found to be represented quite satisfactorily by the integrated form of this equation, $k_1(1-\eta a)=1/t\,.\,\log a(1-\eta x)/(a-x)$, in which $\eta=k_2/k_1$. The nature of the retarding autocatalytic action has not been established, but it is suggested that it may consist in a diminution of the rate of diffusion brought about by the absorbed substance.

From an examination of earlier experiments in which the kinetics of other sorption processes have been investigated, it is found that the data cannot in general be represented by the simple equation $dx/dt=k(a-x)$. H. M. D.

Kinetics of Adsorption. R. Marc (*Zeitsch. Elektrochem.*, 1914, **20**, 515—524).—Experiments are described on the adsorption of dilute solutions of gum arabic and starch by strontium and barium carbonate under varying conditions of stirring. The solutions were agitated by a rotary stirrer, which made from 100 to 2000 revolutions per minute, and the high rotation experiments were effected under a pressure of 10—15 atms. of nitrogen. The apparatus was so constructed that small portions of the solution could be instantaneously removed from the reaction mixture and analysed by a Zeiss interferometer. It is shown that with rapid stirring the velocity of adsorption increases with the intensity of the stirring, and when the number of rotations is 1800—1900 per minute the adsorption equilibrium is reached in less than six seconds. From the adsorption-time curves it is shown that adsorption does not follow the proportionality law, but in the first few seconds it is rapid, as shown by the rapidly rising curve; it then slowly approaches the equilibrium value, as shown by a bend in the curve and then a slow rise. Equations are deduced which represent the adsorption, and the results calculated from these compared with the experimental results. The adsorption velocity, as well as that of all heterogeneous processes, is shown to be conditioned by the diffusion, and to be dependent on the number of rotations of the stirrer per unit of time. By diffusion, however, is to be understood, not a free diffusion through an undisturbed layer, but a diffusion brought about by an attractive force. J. F. S.

Influence of the Nature of the Adsorbent in Adsorption from Aqueous Solution. H. Freundlich and A. Poser (*Koll. Chem. Beihefte*, 1914, **6**, 297—328).—In view of the fact that the majority of previous observations on adsorption from solution have been made with some form of charcoal, experiments were planned with the object of determining the influence of the nature of the adsorbent on the phenomenon. For this purpose comparative experiments were made with alumina, bole, and animal charcoal. The choice of these substances was partly determined by the fact that alumina becomes positively and bole negatively charged in contact with solution, whilst animal charcoal shows no appreciable

contact potential. The adsorbed substances consisted for the most part of basic and of acid dyes, and of salts of the alkaloids and certain other organic bases.

In nearly every case the variation of the quantity of adsorbed substance with the concentration of the aqueous solution can be represented by means of the usual adsorption equation. The quantity of strychnine nitrate taken up from solution by bole and animal charcoal is, however, nearly independent of the concentration, and the adsorption equation is not applicable in this case.

The assumption that a positive adsorbent will adsorb only acid dyes and a negative adsorbent only basic dyes is shown to be at variance with the results obtained. There is undoubtedly a preferential adsorption in the above sense, but basic dyes are adsorbed by positive alumina to quite an appreciable extent.

The negative colloid arsenious sulphide is adsorbed by positive alumina; the positive colloid ferric hydroxide is similarly adsorbed by negative bole, and both colloids are adsorbed by neutral charcoal. In all three cases, the quantity of adsorbed colloid is independent of its concentration in the aqueous layer.

Some experiments were also made with aqueous solutions of benzoic and of salicylic acid, and with solutions containing both these acids. Each acid is adsorbed from the mixed solutions in accordance with an exponential equation, and the total acid adsorbed is found to be practically equal to that which would be adsorbed from a solution of either of the acids the concentration of which is equal to that of the mixture. H. M. D.

The Adsorption Capacity of Talcs and Kaolins. PAUL ROHLAND (*Kolloid. Zeitsch.*, 1914, **15**, 180—182).—Talcs and kaolins are capable of adsorbing considerable quantities of dyes from aqueous solutions. The adsorption capacity depends on the colloid nature of the talc or kaolin, and the more pronounced this is, the greater is the adsorption capacity. The results obtained with talc show, further, that, in general, the extent to which dyes are adsorbed increases with the colloid character of the dye. The adsorption power may therefore be employed in differentiating between crystalloid and colloid dyes. Since certain dyes yield molecular disperse systems in dilute solution and colloid systems in more concentrated solution, the adsorption capacity may also be used in the investigation of the transition from the crystalloid to the colloid condition.

Since the adsorption capacity of the kaolins, as well as the plasticity and the readiness with which they adhere to vegetable fibres, are dependent on the colloid character of the kaolin, it is evident that their behaviour towards organic dyes may be usefully employed in forming an estimate of the suitability of the kaolins for use in the ceramic and paper industries. H. M. D.

Adsorption and the Surface Tensions of Aqueous Solutions of Homologous Fatty Acids and Alcohols. MARKS NEIDLE (*J. Amer. Chem. Soc.*, 1915, **37**, 513—515).—Morgan and Neidle (A.,

1914, ii, 33) have determined the surface tensions of aqueous solutions of methyl, ethyl, and amyl alcohols and of formic and acetic acids, and have confirmed the Duclaux relationship for these substances.

A physico-chemical interpretation of the Duclaux equation has now been deduced, which leads to the conclusion that in dilute aqueous solutions of the fatty acids the adsorption at a given temperature and surface tension is inversely proportional to the van't Hoff factor, but that it is the same for homologous aliphatic alcohols. E. G.

Adsorption. XI. Hysteresis of the Extent of Hydration of Cellulose. A. V. Rakovski (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 18—21. Compare A., 1914, ii, 434).—The author has investigated, by van Bemmelen's method (A., 1911, ii, 470), the chemical hysteresis of cotton-wool, filter-paper, flax, and hemp at 19°, the last two having been previously washed successively with water, alcohol, ether, alcohol, and water. The curves connecting vapour pressure with the proportion of water present are almost coincident for filter-paper and cotton-wool, but at pressures exceeding 12 mm. the former contains rather more water than the latter. For the conditions employed, the velocity of adsorption is greater than for starch, the attainment of equilibrium occupying five to seven days, or, for pressures above 14 mm., three to five days; in a desiccator containing 1% sulphuric acid solution the establishment of equilibrium is doubtful. In general, dehydration proceeds more slowly than hydration. The hysteresis exhibits a maximum of 1·8% of water, and is somewhat less than with starch. Separate calculation of the hydration and dehydration results obtained by Masson and Richards (*Proc. Roy. Soc.*, 1907, [*A*], **78**, 412) for cotton-wool and filter-paper shows them to be in very fair agreement with those obtained by the author. T. H. P.

Adsorption and Capillarity from the Point of View of the Second Law of Thermodynamics. M. Polànyi (*Zeitsch. physikal. Chem.*, 1914, **88**, 622—631).—A theoretical paper in which the following points are considered mathematically: (1) The influence of the swelling of a colloid and adsorption; (2) adsorption in colloidal solutions and the effect on osmotic pressure; (3) the freezing point of the solvent taken up in the gel; (4) adsorption isothermals and the electro-potential curves; (5) mutual repulsion of adsorbed substances; (6) the surface tension at the boundary of two liquids; and (7) mutual repulsion of liquids at solid surfaces. J. F. S.

The Change from Ordered to Turbulent Flow in Capillary Tubes. I. Walther Sorkau (*Physikal. Zeitsch.*, 1914, **15**, 768—772).—A series of viscosity measurements have been made with benzyl alcohol under various pressures and at temperatures from 25° to 50°. The absolute viscosity-coefficient has been calculated in each case, and the following values found: 25°, 0·05054;

30°, 0·04326; 35°, 0·03739; 40°, 0·03288; 45°, 0·02906; and 50°, 0·02574. The critical pressure and critical time for non-turbulent flow are calculated for each temperature. It is shown that the value of the velocity necessary to change non-turbulent flow into turbulent flow decreases with increasing temperature. The critical velocity is given by the formula $U_{crit.}=V/t\,.\,q$, where V is the volume of liquid passed through, q the area of the capillary, and t the time. The Reynolds' constant K is calculated for each temperature from the formula $K=rDU_{crit.}/\eta$, where D is the density of the benzyl alcohol, η the viscosity-coefficient, and r the radius of the capillary. J. F. S.

Liebig's Views on Osmotic Pressure. I. P. Osipov (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 26—29).—The author urges the recognition of von Liebig's work on osmosis, which is referred to only cursorily in such standard text-books as Ostwald's "Lehrbuch der Allgemeinen Chemie" and Chvolson's "Physics." T. H. P.

Influence of Sucrose and Alkali Chlorides on the Solvent Power of Water. J. C. Philip and A. Bramley (*T.*, 1915, **107**, 377—387).—The solvent power of water is influenced by the presence of either electrolytes or non-electrolytes, and the suggestion has previously been developed that this is due to the hydration of the added substance (T., 1907, **91**, 711). Experiments have now been carried out with the object of ascertaining how the magnitude of this effect varies with the nature of the added substance, and how far it is independent of the non-electrolyte employed in measuring the solvent power of the water. The distribution method was employed, the variation in the partition-coefficients of ethyl acetate, phenol, and acetone between benzene or petroleum and aqueous solutions of sucrose or alkali chlorides being determined. The results obtained with sucrose solutions emphasised the conclusions previously reached (*loc. cit.*) that non-electrolytes can influence the solvent power of water, and that the phenomenon is not an ionic function as maintained by Levin (A., 1906, ii, 527). The "equivalent relative lowering of solvent power" was found to increase with the dilution in every case, and since this was observed with varying solutes, the effect is due to a factor involving only sucrose and the water, which becomes relatively more important as the proportion of water increases. The hypothesis of the hydration of the sucrose fulfils these conditions, and calculations based on the values observed would give a molecular hydration from 6·5 in concentrated solutions to 11 in the dilute solutions. Of the results obtained with the alkali chlorides those with sodium chloride are regarded as the most trustworthy, and with it the values obtained for the lowering of the solvent power were the same for both ethyl acetate and phenol, thus affording evidence that the values obtained with either of these distributed substances were a real measure of the extent to which the solvent power of the water had been affected by the sodium chloride. The agreement in the case of potassium and lithium chlorides was not so good, probably owing to

their quite appreciable solubility in the distributed substances, which naturally produces disturbing influences in the partition-coefficients. Of the three reference substances used, acetone was the least satisfactory in every case, since all the alkali chlorides are distinctly soluble in it. On the assumption that the lowered solvent power of water is due to the hydration of the molecules and ions in solution, it is calculated that the average molecular hydration of sodium chloride lies between 9·5 (for 4*N*-solution) and 17·8 (for 0·5*N*-solution), and of potassium chloride 8·6 and 16·4 for solutions of the above strength. G. F. M.

Physico-chemical Studies of Solutions of Palmitates. KURT ARNDT and PAUL SCHIFF (*Koll. Chem. Beihefte*, 1914, **6**, 201—230).—As a means of contributing to a knowledge of the properties of soap solutions, the authors have investigated the electrical conductivity and the viscosity of 0·1*N*- and 0·01*N*-solutions of sodium and potassium palmitate at temperatures between 25° and 85°. Observations were also made in order to elucidate the nature of the coagulation process. The coagulated soap consists of a mixture of acid and normal palmitate, the composition of the mixture varying with the concentration of the solution. The coagulation process consists in the reversible transformation of the sol into the gel form, but equilibrium is only attained very slowly. For this reason, differences in the electrical conductivity at a given temperature are usually found, according to whether the palmitate solutions are cooled on the one hand, or whether the gel forms are raised to this temperature on the other.

The coagulation temperature depends, not only on the concentration of the solution, but also on the nature of the cation. For the sodium salt, the temperatures are about 30° higher than for equally concentrated solutions of the potassium salt. Differences are also found in the effect produced by the addition of the corresponding chlorides, in that the addition of an equivalent quantity of sodium chloride to a 0·1*N*-solution of sodium palmitate raises the coagulation temperature by 7°, whilst the addition of potassium chloride to a solution of potassium palmitate has no appreciable effect on the coagulation process. H. M. D.

Metastable Continuation of the Fusion and Mixed Crystal Curves, and the Connexion between Monotropy and Enantiotropy. A. SMITS (*Zeitsch. physikal. Chem.*, 1915, **89**, 257—270).—A theoretical paper in which a number of possibilities, concerning the continuation of the fusion and mixed crystal curves of binary systems, are considered. From the considerations it follows that a temperature boundary exists for a solid substance, and if this is the case it follows that a similar limiting temperature must exist for the co-existence of two solid substances. The transition from the monotropic condition into the enantiotropic condition is considered, and it is shown that the conditions of the transition are deducable in a simple manner from the theory of allotropy. It is also shown that the transition curve can commence at the meta-

stable transition point, or at a point where the co-existence of the two solid phases becomes possible. It is also shown that the metastable fusion curve does not always meet the vapour-pressure curve of the liquid, so that a triple point, solid–liquid–vapour, appears. The metastable fusion curve can either continue to the absolute zero, without meeting the vapour-pressure curve, or it can take its origin at some higher temperature. This means that whilst it is possible for monotropy to be absent under the vapour pressure of the system, yet under higher pressures enantiotropy makes its appearance. J. F. S.

Liquid Crystals and Colloids. O. LEHMANN (*Kolloid. Zeitsch.*, 1914, **15**, 65—75).—An account is given of the observations which led to the elucidation of the nature of liquid crystals. Although the liquid crystal state would appear to resemble the colloidal state in certain respects, the anisotropy associated with the former affords a certain criterion for differentiating between the two. The closer investigation of many substances classified as colloids will probably show that some of them belong to the group of liquid crystals. H. M. D.

The Colloid Chemistry of Indicators. A. HANTZSCH (*Kolloid. Zeitsch.*, 1914, **15**, 79—83).—According to Ostwald (A., 1912, ii, 439), the changes of colour of indicators in acid and alkaline solution are in many cases attributable to changes in the degree of dispersity. The author contends that the observations which are brought forward as evidence in support of this view are due to the presence of foreign substances in the commercial indicators employed. Chemically pure helianthin, methyl-orange, and Congo-red do not yield colloidal solutions under the conditions in which they are employed as indicators, and it is probable that the colloidal character of solutions of many others is entirely due to impurities. It is shown, further, that the colloid condition plays no part in the colour changes of indicators in ordinary circumstances. Such colour changes are quite different from the changes which are exhibited by colloidal metals, and can in all cases be satisfactorily interpreted on chemical grounds in terms of two or more isomeric forms which have different colours. H. M. D.

The Colloids in Pyridine. A. PIERONI and E. GIRARDI (*Kolloid. Zeitsch.*, 1914, **15**, 159—164).—The author describes the preparation of colloidal solutions of metals in pyridine by the interaction of metallic salts with pyrogallol in pyridine solution, followed by the addition of water. The metallic salts used were silver nitrate and acetate, mercuric chloride and acetate, cupric chloride, nitrate and acetate and nickel chloride, nitrate and acetate. Differences in behaviour, as shown by the quantity of water which must be added to bring about coagulation, are mainly determined by the acid radicle. The chlorides of the different metals exhibit close similarities in behaviour, and this is also true for the nitrates and for the acetates of the various metals. H. M. D.

Measurement of the Protective Action of Protective Colloids. JULIUS GRÓH (*Zeitsch. physikal. Chem.*, 1914, **88**, 414—418).—The action of protective colloids on colloidal platinum is determined by measuring the rate of decomposition of hydrogen peroxide by colloidal platinum with and without the addition of a protecting colloid. The author measures the time required for the decomposition of 50% of the hydrogen peroxide. The following results are obtained for the action of gelatin: unprotected colloid decomposes 50% of the hydrogen peroxide in thirty minutes, and addition of 0·001% gelatin increases the time to 131 minutes; 0·01% gelatin, 138 minutes; 0·05% gelatin, 186 minutes; and 0·10% gelatin, 295 minutes. In alkaline solution the protective action is not so marked, the rate of decomposition being reduced only about one-third. Comparative measurements are made of the protective action of gelatin, gum arabic, and dextrin. The order of protective action is that given above, and it persists for all concentrations from 0·1% to 0·0001%, the relative values being approximately the same as those found by Zsigmondy by means of the gold numbers. J. F. S.

Emulsions. Adsorption of Soap in the Benzene–Water Interface. T. R. BRIGGS (*J. Physical Chem.*, 1915, **19**, 210—231).—A theory, based on the Gibbs' equation, $u=-c/RT\,.\,d\sigma/dc$, for the relationship between the surface tension of a solution and the distribution of a dissolved substance between the body of a solution and the interfacial film, is developed for the concentration of a dissolved substance in gas-liquid layers and liquid-liquid surface layers. These two cases exist in foams and in emulsions respectively. The latter case is experimentally investigated in the case of sodium oleate solutions. Solutions of sodium oleate in water are shaken with benzene until the latter is completely emulsified; then, after keeping until a separation into two layers has taken place, the aqueous layer is analysed, and the change in concentration noted. It is shown that the amount of sodium oleate removed from the solution is dependent on the concentration of the solution and on the specific surface of the benzene phase. The amount of soap removed increases rapidly at first with small increases of concentration of the solution, and then remains very nearly constant while the concentration of the solution undergoes great change; in this respect a strong similarity to ordinary adsorption is shown. The results are only partly in accord with Freundlich's equation, $x/m=ac^{1/n}$, in which x/m is the amount of substance adsorbed by unit mass of adsorbent, c is the equilibrium concentration of the substance in solution, and a and $1/n$ are constants depending on the nature of the substances present. A device is described for preparing homogeneous emulsions. J. F. S.

The Action of Electrolytes in the Formation and Inversion of Oil–Water Systems with Certain Biological Applications. G. H. A. CLOWES (*Kolloid. Zeitsch.*, 1914, **15**, 123—126).—When olive oil is shaken with very dilute sodium hydroxide, emulsions

are formed, in which the oil forms the disperse phase. If the emulsions are shaken with a solution of calcium chloride the concentration of which exceeds that of the sodium hydroxide, they are transformed into emulsions of opposite character in which the water forms the disperse phase. In presence of equivalent amounts of calcium and hydroxyl ions, the tendency towards the formation of the two kinds of emulsion is almost the same, and the system is in a sort of critical condition, in which the directive action of the calcium ions is counterbalanced by the action of the hydroxyl ions. It is probable that the activity of these ions is due to adsorption, for there is evidence of a close connexion between this and other phenomena which are conditioned by the adsorption of ions.

The antagonism shown by the positive and negative ions has been further investigated in experiments with mixtures of solutions of calcium chloride and sodium citrate, in which the influence of the calcium ion is counteracted by that of the citrate ion. From observations on the stability of oil–water emulsions on the addition of solutions containing the two active ions in different proportions, it is found that there is no coagulating effect exerted by the added solution when the calcium and citrate are in the ratio of 1 : 2. This particular solution is also inactive when injected intravenously into mice, and it has no influence on the hæmolysis of blood corpuscles, although positive effects are produced by solutions in which ratio is different from 1 : 2.

Further experiments afford evidence that the coagulation of blood is primarily determined by the liberation of thrombin in consequence of a disturbance in the equilibrium of the cell membrane as a result of the adsorption of ions. H. M. D.

Diffusion of Electrolytes and Formation of Precipitates in Jellies. B. L. Vanzetti (*Zeitsch. Elektrochem.*, 1914, **20**, 570—579).—The rate of diffusion of hydrochloric acid, hydrobromic acid, hydriodic acid, and nitric acid of 0·1*N*-strength in gelatin of 5% concentration has been determined at 18°. The diffusion was followed in some cases by means of indicators, and in others by means of a slight change in the colour of the gelatin. In one series of experiments the gelatin solution contained silver nitrate in sufficient quantity to make a 0·1*N*-solution. It is shown that the diffusion is in accord with Fick's law, and that in the case of the various acids the rate is almost proportional to the migration velocity of the anions. The same is also true for the slower diffusion of the insoluble silver salts formed in those cases where the gelatin contained silver nitrate. In these cases nitric acid is formed which diffuses above the precipitate of silver haloid, and reaches nearly the same height as the halogen acids in gelatin free from silver nitrate. Nitric acid diffuses somewhat more quickly in the presence of silver nitrate than in its absence. The relationship $Height/(Time)^{\frac{1}{2}}$ is constant in all cases, both for the halogen acids and the silver haloids, although the value of the constant differs with the concentration of the acids. The relationship

$$Height\ (Acid)/Height\ (Silver\ Salt)$$

was constant throughout the experiment. On changing the concentration of the silver nitrate in the gelatin, the height (h_1) reached by the acid in a given time remains constant, but the height, h, reached by the silver salt changes in the sense that the ratio h_1/h tends to approach unity with decreasing silver nitrate concentration. Within definite limits, with the same concentration of silver nitrate, the relationship h_1/h is independent of the strength of the acid. The observation of Liesegang ("Chemische Reaktionen in Gallerten," Düsseldorf, 1898), that in the diffusion of halogen salts in gelatin containing silver nitrate the height of the insoluble salts at high dilution is the same, is explained as due to the back diffusion of the soluble silver salt. J. F. S.

The Action of Alkali Silicates on Clay and Kaolin Suspensions. P. Rohland (*Kolloid. Zeitsch.*, 1914, **15**, 158—159).—If a small quantity of a solution of an alkali silicate is added to a suspension of raw kaolin, the particles of quartz and sand are found to separate out very quickly. Various observations show that this cannot be attributed to the influence of the colloidal silicic acid or the hydroxyl ion which are formed as a result of the hydrolysis of the silicate, but must be ascribed to the action of the undissociated alkali silicate in the colloidal state. This action results in an increase in the degree of dispersity of the kaolin particles, and the settling out of the quartz and sand particles is a consequence of this physical change. H. M. D.

Precipitation and Peptisation of Albumin Sols by Colloids Suspended in Solutions of Electrolytes. A. Brossa and H. Freundlich (*Zeitsch. physikal. Chem.*, 1915, **89**, 306—337).—A large number of experiments on the precipitation of electrolyte-free albumin sols by colloids and other materials have been carried out. It is shown that albumin sols prepared from ox serum and free from electrolytes possess a negative charge, and are not precipitated by salts of the heavy metals, such as ferric chloride, zinc sulphate, and mercuric chloride. The precipitation of albumin solutions by a positive ferric hydroxide sol or a negative molybdenum dioxide sol decreases with decreasing electrolyte concentration of the solution, and eventually only a faint turbidity is produced, which re-dissolves when a further quantity of the precipitating sol is added. The colloidal solutions obtained by adding ferric hydroxide sol to an electrolyte-free albumin sol were examined, and it is shown that the albumin-ferric hydroxide particles are charged positively, but not so strongly, as the pure ferric hydroxide particles. The ferric hydroxide-albumin sol therefore behaves as a positive suspensoid, which is precipitated by small concentrations of electrolytes. In the precipitation by electrolytes the nature of the anion, its valency, and tendency to adsorption are of importance. The quantity of electrolyte necessary to precipitate the complex sol is much less than that required to precipitate the pure ferric hydroxide sol; consequently the complex sol has become more sensitive. The sensitiveness can be

further increased by adding albumin solution to the albumin-ferric hydroxide sol. With large concentrations of electrolytes, the particles first precipitated are redissolved; in this case, as in the peptisation of globulin and casein sols, the nature of the anions is determinative, in so far as the high valency anions and organic anions (for example, SO_4'', picration, citrate ion) show their action at much smaller concentrations than the others. Albumin is not quantitatively combined with the ferric hydroxide sol, but divided between the sol and the solution. The partition does not follow a simple adsorption isotherm, but the quantity adsorbed is proportional to the concentration for small albumin concentrations, whilst at high concentrations a saturation value is reached. The adsorption does not appear to be reversible. With increasing concentration of ferric hydroxide, the sensitiveness of the complex sol decreases, and approaches more nearly the pure ferric hydroxide sol in properties. The albumin-ferric hydroxide sol is somewhat more turbid than the ferric hydroxide sol, but it cannot be resolved into its constituents in the cardioid ultra-microscope. This is easier in the region where no precipitation is possible, and most easy in those sols to which an excess of albumin solution has been added. The whole of the phenomena of precipitation and re-solution are explained by the adsorption of the anions of the solutions, and depend on the discharge and then re-charging of the particles. If instead of adding an electrolyte to a ferric hydroxide-albumin sol an albumin sol containing an electrolyte is precipitated with ferric hydroxide sol, it is seen that in many respects the relationships are identical, particularly in the amount of ferric hydroxide combined with the albumin. Differences noticeable in the nature of the precipitation can be explained by assuming that the changed conditions have affected the rate of coagulation. J. F. S.

Equation of Condition of Gases and the Quantum Hypothesis. O. Sackur (*Zeitsch. Elektrochem.*, 1914, **20**, 563—570).—The author has deduced an equation of condition for gases on the basis of the quantum hypothesis, which shall be in accord with the behaviour of gases at low temperatures and pressures. To test the validity of the equation, a number of measurements of the change of PV with pressure have been made with the gases oxygen, hydrogen, nitrogen, and helium at various temperatures. J. F. S.

The Co-existence of Phases Subjected to Different Pressures. Paul Niggli (*Zeitsch. anorg. Chem.*, 1915, **91**, 107—133).—A discussion of the application of the phase rule, and of the conception of the thermodynamical potential, to systems in which the pressure is not uniform. Such cases arise in a single gaseous or liquid phase through the action of gravitational or centrifugal forces, or in a gas-liquid system through surface forces. The case of the solid-liquid system has been very fully discussed in reference to ice and water, and has been further considered in reference to metals and rocks by Johnston (A., 1912, ii, 129), Johnston and Adams (*ibid.*, 537), and Niggli and Johnston (A., 1914, ii, 377).

Three principal cases are now considered: (1) solid and liquid are under equal hydrostatic pressure; (2) the solid is under a greater hydrostatic pressure than the liquid; (3) the liquid is under a small hydrostatic pressure, whilst the solid is in a state of strain due to external forces.

An excess of pressure on the solid always lowers the melting point, and increases the solubility of the solid phase. A cube of isotropic solid material under stress cannot have the same solubility on all faces. The higher stress corresponds with a higher potential, and thus with a greater lowering of melting point and a greater solubility. These conclusions are applied to the crystallisation of metamorphic rocks. C. H. D.

Ionisation Equilibrium. JAMES KENDALL (*J. Physical Chem.*, 1915, **19**, 193—209).—The dissociation of electrolytes is theoretically considered. With regard to the abnormalities of electrolytes two classes are differentiated: (1) those connected with strong electrolytes (that is, highly dissociated substances), and (2) those connected with concentrated solutions. The dissociation constants of cyanoacetic acid and dichloroacetic acid are determined at 25°, and it is shown that the dissociation constant obtained experimentally is identical with that calculated from the formula:

$$\gamma^2/(1-\gamma)v = k + c(1-\gamma)/\gamma,$$

where k is the dissociation constant from the Ostwald dilution law, and c a constant. It is found that c increases with the strength of the acid, and in the case of strong electrolytes becomes so large that k is negligible, whereas with weak acids c is so small that it becomes negligible, and the expression reduces to the Ostwald dilution law. With regard to the anomaly of concentrated solutions it is shown that if the concentration of the solvent c_s is introduced and the Ostwald dilution law modified to $c_i^2/c_v = kc_s$, the expression holds for concentrations up to half normal. This is shown in the case of propionic acid and butyric acid. The rôle of the solvent in ionisation is next considered. The idea is developed that dissociation is due to the influence of unsaturated solvent molecules on the molecules of the dissolved substance. The charge on the ions is assumed to come from the solvent reaction:

$$(H_2O)_n^{\pm} \rightleftarrows (H_2O)_{n-1}^{\pm} + H_2O^{\pm}.$$

The larger the associated molecules, the further apart are the free positive and negative charges, and consequently the smaller their mutual attractions, and presumably the stronger the ionising power of the solvent. J. F. S.

Equilibrium in the System, Water–Alcohol. N. A. PUSCHIN and (Mlle.) A. A. GLAGOLEVA (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 100—113).—The temperatures at which alcohol and ether crystallise differ, not by 0·3°, as was stated by Ladenburg and Krügel (A., 1899, ii, 545) and by Guttmann (A., 1907, i, 458), but by 7·1°, and assuming the accuracy of Guttmann's value, −117·6°, for the temperature of crystallisation of ether, that of alcohol will be −110·5°. Addition of water up to 15 mol. % lowers the solidifying

point to the eutectic point, −118°, at which the two straight lines constituting the diagram, meet. In crystalline alcohol, water forms solid solutions with a limiting concentration of 15 mol. %, but alcohol does not give solid solutions with ice. Alcohol and water form no definite compound in either the crystalline or the liquid phase. The molecular depression of the freezing point of alcohol, calculated on 1000 grams of the solvent, and measured by means of benzene and chloroform as solutes, has the value approximately 3. For dilute solutions of water in alcohol the corresponding value is 1·9. T. H. P.

Critical End Points and the System Ethane–Naphthalene. [Miss] ADA PRINS (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1095—1106).—In the course of an investigation designed to find a system analogous to the ether–anthraquinone system which shows two critical end-points (Smits, A., 1905, ii, 234), a number of binary systems were examined. These include (1) ether–alizarin, for which the first critical end-point p was found to be 196·4° and 37·5 atms. The second point, q, could only be approximated to 258° on account of the impossibility of observing the meniscus in the dark red mass. (2) Ether–hexachlorobenzene; in this case the solubility appeared to be so great that the three-phase curve does not meet the plait point curve. (3) Ether–*iso*phthalic acid; the point p lies at 196·1° and 36·8 atms., but q could not be determined on account of the decomposition of the acid. (4) Hexane–anthraquinone; this system shows no critical end-points. (5) The systems naphthalene–carbon dioxide and diphenyl–carbon dioxide both show the point p, but in both cases the three-phase curve starting from the triple point of the solid substance had a steep rise which led to the conclusion that the systems were analogous to the system diphenylamine–carbon dioxide. Finally, the system naphthalene–ethane was investigated. The following data were first obtained: critical temperature of ethane, 32·32°; critical pressure, 48·13 atms. The point q lies at 57·4° and 124·8 atms., and p at 39·40° and 52·89 atms. The full diagram of the equilibrium is given for the system along with the details of all the peculiar points. J. F. S.

Avidity Determinations in Non-aqueous Solutions by the Polarimetric Method. II. Acids. E. RIMBACH and H. HORSTERS (*Zeitsch. physikal. Chem.*, 1914, **88**, 271—290. Compare A., 1911, ii, 869).—A series of avidity determinations have been made in 98% alcohol solution for the following acids: benzoic; *o*-, *m*-, and *p*-hydroxybenzoic; *o*-, *m*-, and *p*-chlorobenzoic; *o*-, *m*-, and *p*-bromobenzoic; *o*-, *m*-, and *p*-nitrobenzoic; *o*-, *m*-, and *p*-aminobenzoic; *o*-, *m*-, and *p*-toluic; 2:4-dinitrobenzoic; and 3:5-dinitrobenzoic acid. The method consists in allowing the acid in question to compete with an optically active acid for an optically inactive base in a polarimeter tube, and from the change in the angle of rotation calculating the partition of the base between the two acids. In the present experiments *d*-mandelic acid was used as the com-

parison acid, and piperidine as the base. A number of corrections have to be applied to the experimental figures to compensate for the influence of the various substances on the rotation of mandelic acid. In other respects the method is the same as that previously employed for bases (*loc. cit.*). The avidity of both acids and bases in alcoholic solution corresponds with the values in water solution. Many of the anomalies which occur in water solution are not found in alcohol solution. It is shown that during the period required for the determination there is no formation of esters by the solvent and the acids employed. J. F. S.

Velocities of Flame in Mixtures of Methane and Air. II. ALBERT PARKER (*T.*, 1915, **107**, 328—337).—In continuation of the work of Parker and Rhead (T., 1914, **105**, 2150), a study has been made of the velocities of flame in mixtures of methane and air in glass tubes with internal diameters of 1·25, 2·65, 5·15, and 9·0 cm., and in an iron tube, 17·5 cm. in diameter. The measurements were made by a slight modification of Parker and Rhead's method, and the mixtures contained from 5·7% to 12% of methane. Curves of the initial velocities, constructed by plotting percentages of methane against initial uniform velocities, show that the velocities increase considerably with the diameter of the tube, and that the limiting diameter cannot be less than 17·5 cm. The probable value of the limiting diameter is not much above 20 cm., but in a tube of this size the velocity is only 1% greater than in a tube of 15 cm. diameter.

Experiments are described which show that by using different coils, different initial velocities are obtained, and that a variation in the type of spark also affects the initial velocity. It is pointed out that in order to obtain the normal initial velocities in mixtures of methane and air, it is necessary that the source of ignition should give no impetus to the propagation. An electric spark seems to induce a more rapid initial inflammation than other modes of ignition, such as adiabatic compression, and it is possible that the initial inflammation induced by a spark will always travel above the "normal" velocity.

A reply is made to Wheeler's criticism (T., 1914, **105**, 2613) of Parker and Rhead's paper (*loc. cit.*). E. G.

Relationship between Electrolytic and Pure Chemical Processes. III. D. REICHENSTEIN (*Zeitsch. Elektrochem.*, 1914, **20**, 406—417. Compare A., 1914, ii, 23).—In a previous communication it was shown (*loc. cit.*) that passivity of metals is analogous to those chemical reactions which, with increasing concentration of one of the reacting substances, at first show an increasing velocity of reaction, and then a steadily decreasing reaction velocity. A number of such reactions are considered in the present paper, and a mathematical representation of the rate of solution of metals in a mixture of sulphuric acid and hydrogen peroxide is deduced. It is shown that the solution of nickel in such a solution is to be regarded as taking place in the four stages: (*a*) adsorption of

hydrogen peroxide, (*b*) $H_2O_2 \longrightarrow H_2O + O$, (*c*) $2O \longrightarrow O_2$, and (*d*) $Ni + O + 2H^{\cdot} \longrightarrow Ni^{\cdot\cdot} + H_2O$. The reaction *b* takes place slowly; its velocity is of the same order as that of *c* and *d*. The reaction *c* leads to the accumulation of oxygen in the electrode volume. With small concentrations of acid both *b* and *c* bring about a slowly increasing passivity of the metal. A number of experiments are described on the rate of solution of nickel and copper in solutions of sulphuric acid and hydrogen peroxide of varying concentrations. In a solution containing 0·970*N*-H_2O_2 and 0·045*N*-H_2SO_4 nickel becomes passive in ninety minutes, whereas in 0·423*N*-H_2O_2 and 0·057*N*-H_2SO_4 one hundred and seventy minutes are necessary. The constant velocity of solution of nickel, which is independent of the time, can also be reached from the passive side. J. F. S.

Piezochemical Studies. XIII. The Influence of Pressure on the Velocity of Reaction in Condensed Systems. II. Ernst Cohen and H. F. G. Kaiser (*Zeitsch. physikal. Chem.*, 1915, **89**, 338—364. Compare A., 1911, ii, 23; 1913, ii, 687, 690).—The rate of hydrolysis of a 0·01*N*-solution of ethyl acetate by a 0·01*N*-solution of sodium hydroxide has been determined at 2·40° and at pressures varying from 1—1500 atmospheres. The pressure regulator and apparatus is the same as that previously described (*loc. cit.*). A thermostat is described, which is capable of giving a temperature constant to 0·01°. The measurements were made by two methods: (1) a titrimetric method, in which it is shown that similarity of experimental conditions is essential for concordant results, and (2) an electrical method which depends on measurement of the change of conductivity of the solutions. In the former method the solutions have to be removed from the pressure chamber for titration, whilst in the latter the concentration of the solution is determined whilst still under pressure. Both methods give results of the same order of accuracy as that obtained at atmospheric pressure. It is shown that the reaction constant increases with the pressure, and at 1500 atms. pressure is 37·4% larger than at ordinary pressure. The experimental results at the various pressures are obtained from the equation $k_p = a + bp$, and also from the van't Hoff equation, $d.l.k/dp = \text{constant}$. J. F. S.

Kinetics of the Action of Potassium Xanthate on Chloroacetates and Chloroacetamide. Bror Holmberg (*Zeitsch. physikal. Chem.*, 1914, **88**, 385—400).—The velocity of reaction of sodium, potassium, strontium, and barium chloroacetates and chloroacetamide on potassium xanthate has been determined, and also the influence of small quantities of the chlorides of the same metals on the rate of reaction. It is shown that the simple reactions are strictly bimolecular, and are to be represented by the equations:

(i) $'O{\cdot}CO{\cdot}CH_2Cl + 'S{\cdot}CS{\cdot}OEt = 'O{\cdot}CO{\cdot}CH_2{\cdot}S{\cdot}CS{\cdot}OEt$.
(ii) $MO{\cdot}CO{\cdot}CH_2Cl + 'S{\cdot}CS{\cdot}OEt = MO{\cdot}CO{\cdot}CH_2{\cdot}S{\cdot}CS{\cdot}OEt + Cl'$.
(iii) $'O{\cdot}CO{\cdot}CH_2Cl + MS{\cdot}CS{\cdot}OEt = 'O{\cdot}CO{\cdot}CH_2{\cdot}S{\cdot}CS{\cdot}OEt + MCl$,

and (iv) $MO\cdot CO\cdot CH_2Cl + MS\cdot CS\cdot OEt =$
$MO\cdot CO\cdot CH_2\cdot S\cdot CS\cdot OEt + MCl$,
in the case of the chloroacetates, and
(v) $H_2N\cdot CO\cdot CH_2Cl + /S\cdot CS\cdot OEt =$
$H_2N\cdot CO\cdot CH_2\cdot S\cdot CS\cdot OEt + Cl'$,
and (vi) $H_2N\cdot CO\cdot CH_2Cl + MS\cdot CS\cdot OEt =$
$H_2N\cdot CO\cdot CH_2\cdot S\cdot CS\cdot OEt + MCl$,
in the case of chloroacetamide.

The reactions (iv) and (vi) are regarded as taking place very slowly, so that in the case of the chloroacetates it is to be expected that a relationship of the type $C = P + Q(M^{\cdot})$ will exist between the equilibrium constant (C) and the concentration of the metal ion $M^{\cdot}$. In the case of the univalent ions sodium and potassium this equation takes the form $C = 0{\cdot}0151 + 0{\cdot}022M^{\cdot}$, where $M^{\cdot}$ is the concentration of sodium or potassium ions, and in the case of the strontium and barium the expression is:

$$C = 0{\cdot}0181 + 0{\cdot}022[K^{\cdot}] + 0{\cdot}034[Ba^{\cdot}].$$

In the case of chloroacetamide the presence of metal ions does not affect the velocity of reaction. The velocity constant in this case is 0·0952, very much larger than that of the simple chloroacetate reaction, which is 0·0197. J. F. S.

Glycolysis. IV. The Influence of Catalysts on Oxidative Glycolysis. Wilhelm Beysel and Walther Löb (*Biochem. Zeitsch.*, 1915, **68**, 368—401).—The rate of oxidation of dextrose, formaldehyde, and glycollaldehyde by hydrogen peroxide is increased by phosphates. This is a catalysis of the hydroxyl-ion action by the phosphate anions, which are not replaceable by glycine or boric acid anions, even when all solutions employed have the same hydroxyl-ion concentration. The rate can be increased by increasing the concentration of the phosphates, especially when the $[H^{\cdot}]$ concentration exponent is about 7·4—7·5, that is, about that of the blood. Glycine inhibits slightly the oxidation, but boric acid does not. The products of oxidation of the sugar in the presence of phosphates include hydroxy-acids, formic and carbonic acids, formed from the scission products, a pentose and formaldehyde. Formaldehyde and glycollaldehyde behave, as regards the phosphate action, much in the same way as the sugar. S. B. S.

Velocity of Solution of Molecular Layers. Georg von Hevesy and Elisabeth Róna (*Zeitsch. physikal. Chem.*, 1915, **89**. 294—305).—The rate of solution of a mixture of thorium-B and thorium-C has been determined in water, nitric acid of various strengths from $10^{-5}N$ to $1{\cdot}0N$, and in nitric acid containing glycerol. The molecular layer was prepared by allowing thorium emanation to deposit its decomposition products on thin quartz plates. The velocity of solution was determined by measuring the rate of change of the β-activity. It is shown that the rate of solution of molecular layers follows the same laws as layers of finite thickness, thus:

$$dx/dt = D/\delta \,.\, OF(c_0 - c),$$

where δ is the thickness of the surface layer, F the proportionality

factor, D the coefficient of diffusion, O the surface, c_0 the concentration of a saturated solution, and c the concentration of the solution. The rate of solution of lead and bismuth isotopes in nitric acid increases with the concentration of the acid, with decrease in the viscosity, and with the absolute solubility of the salt. The presence of lead ions in the solution decreases the rate of solution of the lead isotope (thorium-*B*) without affecting the bismuth isotope (thorium-*C*). It is shown that the interchange of solid molecules of lead chloride with dissolved molecules can be determined by use of thorium-*B* as an indicator. In an addendum to the paper the solubility of lead chromate is determined, using thorium-*B* as indicator; the value found is $2{\cdot}0 \times 10^{-7}$ gram mols. per litre, a value which is well in agreement with the values found by other methods.

J. F. S.

Influence of Temperature in Acid Catalysis. Hugh Stott Taylor (*J. Amer. Chem. Soc.*, 1915, **37**, 551—557).—A study of recent papers on the catalysis of esters, and especially those of Dawson and Powis (T., 1913, **103**, 2135) and Lamble and Lewis (T., 1914, **105**, 2330), has led the author to the conclusion that the ratio of the catalytic activities of the non-dissociated molecule of the acid and the hydrogen ion does not possess a considerable temperature-coefficient, such as has been suggested by McBain and Coleman (T., 1914, **105**, 1520), but that, on the contrary, it is independent of temperature. This has now been confirmed by determinations of the velocity of hydrolysis of ethyl acetate with 0·1*N*-hydrochloric acid, alone and in presence of potassium chloride at 0°, 25°, and 40°. The importance of a consideration of the activity of the non-dissociated molecule in calculations of reaction constants in acid catalyses is emphasised.

E. G.

Experimental Confirmation of the New Theory of Allotropy IIa. A. Smits and S. C. Bokhorst (*Zeitsch. physikal. Chem.*, 1914, **88**, 608—621. Compare A., 1913, ii, 393, 933).—A number of experimental methods of proving the authors' theory of allotropy are given. These all depend on the effect of a previous treatment on the physical properties of such substances as come within the scope of the theory. A number of examples of such determinations are quoted, which all tend to support the theory. Particular weight is laid on the statement of Benedicks (*J. Iron and Steel Inst.*, 1912, No. 2, 442), in which four types of allotropy are differentiated. These four types are shown by the authors to be in accord with their theory. A number of experiments are described dealing with the different behaviour of white phosphorus after different treatment. Thus the freezing point is shown to depend on the previous treatment. Phosphorus which has been melted and slowly cooled can be kept in a molten metastable condition for several days, whilst phosphorus which has been rapidly cooled solidifies almost at once. These differences are shown to be in keeping with the theory of allotropy.

J. F. S.

The Cyclic Evolution of the Chemical Elements. F. H. Loring (*Chem. News*, 1915, **111**, 157—159).—It is suggested that the evolution of the elements may be represented by means of a cyclic diagram similar in type to the hysteresis curve which shows the changes in magnetism when the magnetising force is periodically withdrawn and re-applied during its general progressive variation. In conformity with Crookes' views of the genesis of the elements, the elements are assumed to be formed where time-breaks occur in the continuity of the flow of energy. These time-breaks correspond with subordinate loops in the general cyclic curve. H. M. D.

Twenty-second Annual Report of the [American] Committee on Atomic Weights. Determinations Published during 1914. Gregory Paul Baxter (*J. Amer. Chem. Soc.*, 1915, **37**, 407—417).—A review of the work published during 1914 on atomic weights, including those of oxygen, nitrogen, chlorine, neon, carbon, sulphur, silver, iodine, barium, nickel, cadmium, mercury, vanadium, tellurium, radioactive lead, uranium, and neoytterbium. E. G.

The Periodic System and Periodicity in Properties. A. Vosmaer (*Chem. Weekblad*, 1915, 263—268).—An essay on the periodic system, giving curves illustrating the periodicity of atomic volume, specific gravity, atomic weight, specific heat, melting point, coefficient of expansion, and specific conductivity. A. J. W.

Dissociation of Hydrogen into Atoms. II. Calculation of the Degree of Dissociation and the Heat of Formation. Irving Langmuir (*J. Amer. Chem. Soc.*, 1915, **37**, 417—458).—Langmuir and Mackay (A., 1914, ii, 717) have measured the losses of heat from tungsten wires in hydrogen at pressures from 0·01 mm. up to ordinary atmospheric pressure. The results of these experiments have now been applied to the calculation of the degree of dissociation and the heat of formation of molecular hydrogen.

It is suggested that the dissociation of the hydrogen does not occur in the space around the wire, but takes place only among the hydrogen molecules which have been absorbed by the metal, and that within the metal the reaction is so rapid that equilibrium may be assumed to prevail at all times. The equilibrium constant within the metal may, however, be different from that in the gas phase. It is assumed that the hydrogen does not have to diffuse through an adsorption film on the surface of the wire, but that absorption takes place by the collision of the molecules or atoms with the surface; a certain fraction, α_2, of the molecules is thus absorbed, whilst the fraction $1-\alpha_2$ is reflected, and similarly of the atoms striking the surface the fraction, α_1, is absorbed. The partial pressure of atomic hydrogen immediately around the wire depends on (1) the rate at which atomic hydrogen escapes from the wire, (2) the rate at which atomic hydrogen is absorbed by the wire, and (3) the rate at which it can diffuse away from the wire.

On the basis of these considerations the following equation has

been developed for the calculation of the dissociation constant, K (in the gas phase):

$$K=[(W/q)^2(P/D+1/\alpha_1)^2]/[P-(W/q)(P/D+1/\alpha_2)],$$

where W is the heat carried from the filament by dissociation, q the heat of reaction, D the diffusion-coefficient, and P the total pressure. The values of K, q, D, α_1, and α_2 which were found to give the best agreement between experiment and theory were as follows: For the dissociation constant $\log_{10}K=7\cdot77-19700/T$, whence it is calculated that the degree of dissociation at 760 mm. is 0·0033 at 2000°, 0·014 at 2300°, 0·031 at 2500°, 0·17 at 3100°, and 0·34 at 3500° (abs. temp.). The heat of reaction at constant volume for $2H=H_2$ is 84,000 cal., or at constant pressure 90,000 cal. at 3000° (abs. temp.). The diffusion-coefficient of atomic hydrogen in molecular hydrogen, D, is found to be $2\cdot14\times10^{-3}T^{\frac{3}{2}}$, which is 4·2 times as great as that calculated previously (A., 1912, ii, 827); this difference is accounted for on the supposition that the hydrogen molecules are more or less "transparent" to hydrogen atoms. The coefficient α_1 has a constant value of 1, whilst α_2 appears to be constant and of the value 0·68, or, in other words, all the hydrogen atoms striking the wire are absorbed by it, and 68% of all the hydrogen molecules are absorbed.

Experiments on the losses of heat from tungsten wires in mixtures of nitrogen and hydrogen give results in harmony with the theory; the diffusion-coefficient of hydrogen atoms through nitrogen is found to be $D=2\cdot5(T/273)^{\frac{3}{2}}$, which agrees well with the value calculated by the kinetic theory. E. G.

The Relative Dimensions of Molecules. A. O. Rankine (*Phil. Mag.*, 1915, [vi], **29**, 552—555).—According to Sutherland the viscosity of a gas is proportional to $T^{\frac{3}{2}}/(1+C/T)$, where T is the absolute temperature and C a constant. In calculating the molecular dimensions from the viscosity, it follows that the molecular radius, as estimated according to the simple kinetic theory, must be diminished in the ratio $(1+C/T)^{\frac{1}{2}}:1$, in order to obtain the true radius.

By making use of the author's data for the viscosity of the halogens and the inert gases, the following values are obtained for the molecular radii: chlorine, 1·60; bromine, 1·71; iodine, 1·88; argon, 1·28; krypton, 1·38; xenon, $1\cdot53\times10^{-8}$ cm. The ratio of the radii for chlorine and argon is 1·25, for bromine and krypton 1·24, and for iodine and xenon 1·23. Assuming that the molecules are spherical, it follows that the halogen molecules have practically twice the volume of the corresponding inert gas molecules.

It is also shown that the ratio of the constant C in Sutherland's equation for corresponding members of the halogen and inert series of elements is constant and equal to 2·3. The constant C, it may be noted, affords a measure of the work done against the attractive forces in separating to an infinite distance two molecules originally in contact. H. M. D.

Molecular Attraction. II. K. K. JÄRVINEN (*Zeitsch. physikal. Chem.*, 1914, **88**, 428—450. Compare A., 1913, ii, 293).—The formula $F=m^2k/r^5$, in which the symbols have the meanings previously given (*loc. cit.*), is accepted for the molecular attraction, and values calculated from the various formulæ derived from it are compared with experimental data. It is shown that this expression only holds for the cases where the middle points of the attraction coincide with the centres of the atoms; in the case of molecular attraction the formula must be changed to one of the form $F=m^2k/(r-br_1)^5$, in which b is a constant, r the distance between the molecules, and r_1 the diameter of the molecules. The formula $C_a/Wia=$constant derived from the above formula (*loc. cit.*) agrees with the experimental values when the theoretical value of the constant is employed, namely, 1·29 for monatomic substances and 1·63 for polyatomic substances. A complicated formula is deduced for the heat of vaporisation at various temperatures; this is shown to agree with fact at temperatures in the region of the critical point. The attraction constant k is calculated for a large number of substances, and it is shown that the product ks is a constant for a large number of substances; s is the density at the boiling point. Associated substances and most inorganic substances, however, do not give constant values. The conclusion is drawn from this that the molecular attraction between equal volumes of all substances is the same, a statement which is taken to point to a uniform material as the basis of all elements.

J. F. S.

New Form of Sulphuric Acid Drying Vessel. EARL OF BERKELEY and E. G. J. HARTLEY (*Phil. Mag.*, 1915, [vi], **29**, 609—613).—In connexion with measurements of the vapour pressure of aqueous solutions by the dynamic method, some experiments have been made which show that moist air can be dried as efficiently by sulphuric acid as by phosphoric oxide. The air need not be bubbled through the acid; it is sufficient to lead the gas over the surface of the liquid. A suitable and efficient form of apparatus is described, which consists of four horizontal tubes each 22 cm. long and 2 cm. internal diameter. These tubes are about half filled with acid, and experiments have shown that the moisture is almost completely absorbed in the first of the four compartments.

A new form of phosphoric oxide tube is also described.

H. M. D.

Safety Arrangement for Working with Poisonous or Odourous Gases. FRITZ HENDEN (*Chem. Zeit.*, 1914, **38**, 1009).—Description of a gas-washing bottle, which is surmounted by a safety bulb into which the washing liquid is driven by the gas in case of a stoppage, and through which the gas itself can escape by means of a safety outlet into the fume chamber. When it is not necessary to wash the gas a slightly modified form of apparatus is available. It then functions practically as a mano-

meter flask, and any slight alteration in the pressure or rate of flow of the gas is immediately obvious by the alteration in the height of the liquid (sulphuric acid, for example) in the tube leading from the flask itself, through which the gas is passing, into the upper safety bulb, and, of course, a complete stoppage would, as with the washing bottle, drive the liquid into this bulb, and eventually permit the gas to escape through the safety outlet.

G. F. M.

A New Blowing Pump. HENRI VIGREUX (*Bull. Soc. chim.*, 1915, [iv], **17**, 41—43).—A description of a simple water-pump capable of delivering air at the rate of 400 litres an hour under a pressure of 110 mm. of mercury with a water pressure of 24 metres. The pump can be adapted for use with comparatively low water pressures.

W. G.

Inorganic Chemistry.

Recent Work in Inorganic Chemistry. JAS. LEWIS HOWE (*J. Amer. Chem. Soc.*, 1915, **37**, 536—549).—A review of the progress made in inorganic chemistry in 1914. E. G.

Firing of Gases by Adiabatic Compression. III. Ignition-points of Mixtures of Electrolytic Gas with Argon. Ratio of the Specific Heat for Nitrogen and Hydrogen. JAMES MURRAY CROFTS (T., 1915, **107**, 290—305).—Dixon and Crofts (T., 1914, **105**, 2036) have described an apparatus by means of which gaseous mixtures may be fired by adiabatic compression. The ignition-points of mixtures of electrolytic gas with oxygen, hydrogen, or nitrogen were calculated from the formula

$$T_2/T_1=(V_1/V_2)^{\gamma-1},$$

where V_1 and V_2 denote the initial and final volumes of the compressed gases, T_1 and T_2 the initial and final temperatures on the absolute scale, and γ the ratio of the specific heat of a gas at constant pressure to that at constant volume. All the gases were diatomic, and for γ the value 1·4 was adopted. The results showed that the addition of hydrogen or nitrogen to electrolytic gas increases the ignition temperature in proportion to the amount of gas added.

The present experiments were undertaken with a view to determine the effect of argon, a monatomic gas, on the ignition-point in comparison with that of nitrogen and that of hydrogen. The ignition-points were calculated on the assumption that in the case of argon $\gamma=1{\cdot}666$. The results were similar to those obtained with nitrogen and hydrogen, the ignition-point being increased in proportion to the amount of argon added. A recalculation of the

ignition-point of electrolytic gas has given the value 520° instead of 526° (Dixon and Crofts, *loc. cit.*). The ignition-points of mixtures, $2H_2+O_2+xA$, are given by the formula $520+13x$.

Since it is probable that nitrogen or excess of hydrogen acts in the mixtures as an inert gas, it may be assumed that the actual ignition-points of these mixtures are close to those found for the corresponding argon mixture. On this basis, values of γ and C_v for nitrogen and hydrogen have been calculated. The mean value of C_v for nitrogen is expressed by the formula $\underset{(15.t)}{C_v}=4{\cdot}7+0{\cdot}0004t$ and that for hydrogen by the formula

$$\underset{(15.t)}{C_v}=4{\cdot}7+0{\cdot}001t-0{\cdot}0000002t^2.$$ E. G.

Firing of Gases by Adiabatic Compression. IV. Ignition-points of Mixtures of Electrolytic Gas with Carbon Dioxide. Ratio of the Specific Heats for Carbon Dioxide. James Murray Crofts (T., 1915, **107**, 306—313).—The work on the firing of gases by adiabatic compression (preceding abstract) has been extended to mixtures of electrolytic gas with carbon dioxide, a triatomic gas. When the values of γ for carbon dioxide, recorded by various authors, are applied to the experimental data, a series of ignition-points is obtained, which do not agree with those obtained from the argon series, and the values for γ and C_v were therefore calculated by the method used in the case of nitrogen and hydrogen (*loc. cit.*).

Experiments carried out to ascertain whether any part of the carbon dioxide is reduced to carbon monoxide on the explosion of the mixture showed that very little, if any, reduction takes place.

The ignition points for mixtures of $2H_2+O_2$ with CO_2, $2CO_2$, $3CO_2$, and $4CO_2$ have been determined, and the values of γ and C_v calculated in each case. The values found for C_v may be expressed by the formula $\underset{(15.t)}{C_v}=6{\cdot}6+0{\cdot}0023t$. E. G.

Iodine Salts. Fr. Fichter and Hans Kappeler (*Zeitsch. anorg. Chem.*, 1915, **91**, 134—144. Compare Kappeler, A., 1912, ii, 39).—[With Eduard Krummenacher.]—*Iodine perchlorate*,

$$I(ClO_4)_3,2H_2O,$$

prepared by dissolving iodine in anhydrous perchloric acid cooled by ice and salt, and oxidising with ozone, separates in greenish-yellow needles, which may be washed with cold perchloric acid. The water arises from the reaction with ozone:

$$I_2+6HClO_4+O_3=2I(ClO_4)_3+3H_2O.$$

Water of crystallisation is also present in basic iodine sulphate. The salt is very readily decomposed by water.

[With Louis Helfer.]—*Iodine sulphate*, $I_2(SO_4)_3$, is prepared by heating the basic sulphate with sulphur trioxide in a sealed tube for one hundred and forty hours at 100—120°. The solid contents are then placed on a porous plate in a vacuum desiccator over sulphuric acid. Yellow crystals are thus obtained.

Iodine iodate, $I(IO_3)_3$, formerly prepared by the action of ozone on iodine, may be obtained by warming iodic acid with concen-

trated phosphoric acid (D 1·70). Oxygen, and then iodine, is evolved, and a yellowish-white precipitate is obtained. It is washed with sulphuric acid and drained on a porous plate.

The supposed compounds HI_7O_3 and $I_2O_4,3SO_3$ have no existence. C. H. D.

A Third and Fourth Variety of Sulphur Molecule. IV. Engel's Sulphur. A. H. W. ATEN (*Zeitsch. physikal. Chem.*, 1914, **88**, 321—379. Compare A., 1914, ii, 121).—As the result of a large number of solubility, transition temperature, density, viscosity, refractivity, molecular weight, and other determinations it is shown that in addition to S_λ, ordinary rhombic sulphur, and S_μ, insoluble amorphous sulphur, two other varieties of sulphur exist which are different from the foregoing either in molecular size or in molecular constitution. Of these one was discovered by Magnus (S_π) and the other by Engel (S_ϕ) (A., 1891, 976). S_π is formed when sulphur is heated at above its melting point and then rapidly cooled. It is also formed by warming solutions of S_λ in sulphur chloride, but in other solvents, such as carbon disulphide, the rate of formation of S_π from S_λ is very slow. Determinations have been made of the amount of S_π formed when sulphur is heated at various temperatures either with or without the addition of 2% of iodine. Solutions of S_π differ from solutions of S_λ in their strong yellow colour. S_ϕ is obtained when a strong solution of hydrochloric acid at 0° is added to a cold solution of sodium thiosulphate and the aqueous solution shaken with toluene. From the toluene solution S_ϕ crystallises after a short time. This form of sulphur is characterised by its orange-yellow colour, and also by its crystal form. Its solutions are yellow-coloured, but not so strongly as those of S_π. The difference of S_π and S_ϕ is definitely proved by the solubility of the two forms. It is difficult to prove the difference of S_π and S_ϕ from S_μ, since S_μ is an insoluble substance, and consequently either S_π or S_ϕ could be identical with S_μ if S_μ exists in an unstable soluble form and the separation of the stable insoluble S_μ takes place slowly. Such a metastable form of S_μ exists. The usual insoluble form of S_μ is not amorphous, but crystalline, and a liquid form of S_μ is also known. It is therefore possible that this liquid S_μ is soluble, and that a solution of S_π or S_ϕ is in reality a solution of liquid S_μ. Against this possibility, however, the following points are conclusive: (1) Amorphous liquid S_μ is insoluble. (2) Crystalline S_μ separates easily from solutions if S_π or S_ϕ is shaken with potassium hydroxide, or when solutions of S_ϕ are shaken with ammonia, or when solutions of S_λ and S_π are submitted to the influence of light. (3) Solutions of S_π in sulphur chloride never deposit S_μ, whereas S_μ is rapidly deposited from a hot solution of S_μ in sulphur chloride on cooling. Hence it follows that S_λ, S_μ, S_π, and S_ϕ represent four different molecules. S_λ is S_8, S_ϕ is S_6, S_π is probably S_4. Solutions of S_π and S_ϕ are stable in the dark, but the addition of S_μ causes a separation of S_μ. The quantity of

S_μ which separates is proportional to the quantity of S_μ added and to the quantity of S_π and S_ϕ present in the solution. The deposition takes place more slowly at 0° than at 25°, and is slower from a solution of S_ϕ than from one of S_π. The separation is much slower from carbon disulphide solutions than from toluene solutions. S_π and S_ϕ are converted partly into S_μ and partly into S_λ on shaking their solutions with potassium hydroxide solution. The same change occurs with ammonia, and the change takes place four times as quickly with S_ϕ as with S_π. If a solution of ammonia in toluene is used, practically no S_μ is formed, but only S_λ, and here also the change occurs four times as quickly with S_ϕ as with S_π. Solid S_ϕ changes slowly in the dark into S_μ and S_λ. The transition takes place more rapidly in the light than in the dark, the amount of S_μ formed being practically the same in both cases, whereas the amount of S_λ is much greater in the light. In a solution of S_ϕ a small deposition of S_μ occurs when submitted to light, but no formation of S_λ. On the other hand S_π is rapidly converted into S_λ on being submitted to light. The density, viscosity, and refractive index of solutions of S_λ, S_π, and S_ϕ differ only slightly from one another. On allowing the three forms to act on silver and mercury, it is shown that S_λ acts most rapidly and S_ϕ more slowly, and that the presence of S_π retards the action of S_λ. During the action on the metals, S_ϕ is transformed into S_λ, and in the same way S_π is transformed into S_λ, but more slowly. In the preparation of S_ϕ in toluene solution, in addition to S_ϕ and S_λ, a further molecular variety is also present. This has temporarily been termed S_x, and in all probability is identical with S_π. J. F. S.

A New Method for the Preparation of Colloidal Selenium. A. Gutbier and Ferdinand Engeroff (*Kolloid. Zeitsch.*, 1914, **15**, 193—201, 210—216).—The action of water on the compounds formed by selenium with bromine has been examined, and it is shown that the decomposition of hydrogen selenium hexabromide, H_2SeBr_6, may be conveniently employed in the preparation of a colloidal solution of selenium.

Selenium bromide, Se_2Br_2, decomposes in contact with water according to the equation $2Se_2Br_2 + 2H_2O = 3Se + SeO_2 + 4HBr$. A small proportion of the selenium passes into solution, but the majority is precipitated. The bromide is apparently unacted on by concentrated hydrobromic acid, but if the acid is gently heated, the selenium bromide dissolves to a small extent, for on cooling and diluting the acid solution, selenium separates out in the colloidal form.

Selenium tetrabromide, $SeBr_4$, dissolves in water, but much more readily in hydrobromic acid, and on dilution of the acid solution, colloidal selenium is formed.

Selenium oxybromide, $SeOBr_2$ (compare Glauser, A., 1913, ii, 403) could not be obtained in pure condition. The substance, prepared according to the method described by Glauser, decom-

poses on contact with water with the formation of a colloidal solution of selenium and the separation of Se_2Br_2 in the form of oily drops.

Hydrogen selenium hexabromide is obtained by the action of bromine on finely divided selenium in presence of concentrated hydrobromic acid (D 1·45). The bromine is added slowly to the mixture, which is kept cool during the reaction. On keeping for some hours, the hexabromide separates in the form of dark red crystals, which dissolve in hydrobromic acid, forming a solution which is quite stable in the absence of light. On dilution of this solution, selenium separates in a colloidal form. The changes taking place may be represented by the equations:

(1) $H_2SeBr_6 + 3H_2O = H_2SeO_3 + 6HBr$,

and (2) $H_2SeBr_6 + H_2O = Se + Br_2 + 3HBr + HBrO$.

The colloidal solution of selenium which is thus obtained may be purified by dialysis. By the addition of 1% of gum arabic the stability of the colloidal selenium is greatly increased. H. M. D.

Anhydrous Hydrazine. II. Electrolysis of a Solution of Sodium Hydrazide in Anhydrous Hydrazine. T. W. B. Welsh (*J. Amer. Chem. Soc.*, 1915, **37**, 497—508).—When anhydrous hydrazine prepared by means of the apparatus described by Hale and Shetterly (A., 1911, ii, 718) is treated with sodium or sodamide, it yields explosive products. Evidence has been obtained of the existence of the hydrazides NaN_2H_3 and $Na_2N_2H_2$.

On the electrolysis of solutions of sodium hydrazide in anhydrous hydrazine, nitrogen and hydrogen appeared at both the anode and cathode. For each atom of copper deposited on the coulometer cathode, 1·1—1·5 atoms of nitrogen were liberated at the anode when the solutions were fairly dilute, but in the case of more concentrated solutions the ratio Cu : N was lower, and had an average value of 1 : 2·4. E. G.

Compounds of Arsenious Oxide. I. The System H_2O–As_2O_3–NH_3. F. A. H. Schreinemakers and Miss W. C. de Baat (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1111—1115).—The equilibrium curves of the system H_2O–As_2O_3–NH_3 have been determined at 30°. From the results it is shown that at this temperature the salt NH_4AsO_2, and probably $NH_4 \cdot H_2AsO_3$, exist. J. F. S.

Colloidal Arsenates. G. Klemp and J. Gyulai (*Kolloid. Zeitsch.*, 1914, **15**, 202—203).—By the successive addition of ammonium sulphate, acetic acid, and excess of sodium arsenate to solutions of zinc, ferrous, manganous, cobalt, cadmium, and calcium salts, colloidal solutions of the arsenates of these metals have been obtained in the form of opalescent jellies. Crystals separate from these jellies when kept for some time. In the absence of ammonium sulphate and acetic acid, the above-mentioned salt solutions yield gelatinous precipitates, but jellies are not obtained under these circumstances. H. M. D.

Flames. Alfred Reis (*Zeitsch. physikal. Chem.*, 1914, **88**, 513—568. Compare A., 1911, ii, 483; 1913, ii, 1050).—The ammonia–oxygen and cyanogen–air and cyanogen–oxygen flames have been very fully investigated. In the case of the first-named flame it is shown that the limits of explosion are above 80% of ammonia and below 15% of ammonia. The temperature of the region between the two zones of the divided flame has been measured by a Holborn-Kurlbaum pyrometer, and the following values obtained: 1 mm. above the inner cone, 1830°; 2 mm. above, 1670°; 10 mm. above, 1400°; 38 mm. above, 1000°; 63 mm. above, 815°. The composition of the gaseous products from the inner cone has been determined, and the decomposition of ammonia in the region between the two cones investigated. A number of similar experiments are described for the cyanogen flames, and it is shown that the combustion of cyanogen in oxygen belongs to the small group of reactions which are uninfluenced by the presence of small quantities of water. Further, in consequence of the diatomic character of the products of combustion in the inner cone, the cyanogen–oxygen flame is to be differentiated from most other flames, and, as a result, has a particularly high temperature, and the gases from the inner cone are very similar to those of the carbon arc flame. The spectra of the inner cone and the space between the two cones of divided flames have been photographed by means of a Hilger quartz spectrograph. These determinations were made for the following flames: cyanogen–oxygen, acetylene–oxygen, coal gas–air, hydrogen–oxygen, and ammonia–oxygen. Diagrams of the spectra are given in the paper, and a discussion of the results entered into, chiefly in respect of the constitution of the material in the space between the zones.

J. F. S.

The Inner Cone of Divided Hydrocarbon Flames. Nicolai Bubnov (*Zeitsch. physikal. Chem.*, 1914, **88**, 641—670).—A series of analyses have been made of the products of combustion from the inner cone of flames, of benzene–air, ether–air, and coal gas–air. The gases for analysis were withdrawn by means of a silver capillary tube from various positions on the outside of the inner cone and at various heights above it. From the results the value of $K = H_2O \cdot CO/CO_2 \cdot H_2$ was calculated. It is also shown that the products of combustion taken from the outside of the base of the inner cone contain oxygen, whereas at the apex of the cone none is to be found. The temperature of the flames calculated from the experiments and those from calorimetric determinations are compared. A further series of experiments have been carried out with cooled coal-gas flames. These have been obtained by using a mixture of air and nitrogen instead of air, and since the temperature of these flames is 150—200° below that of ordinary coal-gas flames, it follows that a dissociation of carbon dioxide cannot take place here. Consequently, the presence of oxygen in the products of combustion is not to be ascribed to the thermodynamic equilibrium, but rather to an incomplete combination in the reaction.

It has been shown that the combustion of carbon monoxide is a relatively slow process, and from the present work it follows that the reaction $2H_2 + O_2$ at relatively low temperatures and oxygen concentrations must take place still more slowly. J. F. S.

Solubility of Carbon Dioxide in Water in the Presence of Starch. ALEXANDER FINDLAY and OWEN RHYS HOWELL (T., 1915, **107**, 282—284).—It has been shown by Findlay and Creighton (T., 1910, **97**, 536) and Findlay and Williams (T., 1913, **103**, 636) that the solubility of carbon dioxide in colloidal solutions is exceptionally high at low pressures, and diminishes with increase of pressure to a minimum or to a constant value. In starch solutions, however, the solubility appeared to increase slightly and continuously as the pressure is increased. The solubility of carbon dioxide in starch solutions has therefore been re-determined at pressures between 260 and 990 mm.

Solutions of soluble starch of 5% concentration and D 1·016 were prepared in three different ways. The results show that the solubility of carbon dioxide is not appreciably affected by differences in the method of preparation of the starch solutions. The solubility decreases as the pressure increases until a maximum is reached at about 760 mm., and then increases slightly. It is therefore evident that starch exerts an influence on the solubility of carbon dioxide similar to that of the other neutral colloids investigated previously. E. G.

The Allotropy of Potassium. I. ERNST COHEN and S. WOLFF (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1115—1118).—Reasoning from the very accurate determinations of the coefficient of expansion of potassium (Hagen, *Ann. Phys. Chem.*, 1883, [iii], **19**, 436), the authors show that potassium can undergo transformation into a second modification, β-potassium, and that the metal as it has hitherto been known is at ordinary temperatures a metastable system in consequence of the presence of both forms at the same time. The transformation into the β-form occurs in the region 59·6—59·8°. J. F. S.

The Binary System Lithium Chloride-Cæsium Chloride. E. KORRENG (*Zeitsch. anorg. Chem.*, 1915, **91**, 194—208. Compare Schemtschuschni and Rambach, A., 1910, ii, 204).—The freezing-point curve of this system has a single eutectic point at 330° and 42 molec. % CsCl. The ascending branch of the curve shows four breaks, corresponding with the compounds LiCl,CsCl, and LiCl,2CsCl, and with the polymorphic changes of the latter compound and of cæsium chloride respectively. These results are confirmed by microscopical examination of thin sections. Both modifications of cæsium chloride are singly refracting. Formation of solid solutions is not appreciable.

The compound LiCl,CsCl melts at 351°, and is optically anisotropic. The compound LiCl,2CsCl decomposes at 380°, and undergoes a transformation at 360°. Both modifications are doubly

refracting. It is distinguishable from the first compound by repeated twinning. Both compounds are highly deliquescent. This is the only system among the alkali chlorides in which compounds are formed. C. H. D.

The Solubility of Silver Chloride. ZBIGNIEW GŁÓWCZYŃSKI (*Koll. Chem. Beihefte*, 1914, **6**, 147—176).—According to Stas's observations on the solubility of silver chloride in water, it would seem that the solubility varies over a wide range according to the method of its preparation. It is probable that such differences in solubility depend on variations in the degree of dispersity of the silver chloride, and in view of the importance of this connexion and the large differences in solubility which are apparently involved, experiments have been made with the object of confirming the results obtained by Stas. These experiments show that the solubility of silver chloride increases with increase in the degree of dispersity, but the observed changes in solubility are very much smaller than those indicated by Stas's experiments. It is suggested that the more soluble forms of silver chloride which were used by Stas were impure, and that the foreign substances present were responsible for the high solubility values obtained. In the author's experiments the solubility was in some cases derived from measurements of the *E.M.F.* of silver concentration cells, and in others the dissolved chloride was estimated by a chemical method. In the application of this method, a litre of the saturated solution was evaporated to dryness after addition of freshly distilled ammonia; the residue was dissolved in a small quantity of a potassium cyanide solution, and the silver deposited from this by electrolysis. The silver was then dissolved in nitric acid, and the solution titrated with 0·01*N*-ammonium thiocyanate.

The solubility of silver chloride which is precipitated from an aqueous solution of the salt by the addition of a concentrated potassium chloride solution is not satisfactorily constant. A much more definite variety is obtained when the silver chloride is precipitated by the addition of dilute potassium chloride.

The solubility of this silver chloride in very dilute solutions of potassium and ammonium chlorides is less than in pure water, but is much greater than that calculated on the assumption that the ionic solubility product has a constant value. H. M. D.

Solubility of Certain Sparingly Soluble Silver Salts. A. THIEL (*J. Amer. Chem. Soc.*, 1915, **37**, 508—510).—The author criticises Hill's paper on the relative solubility of the silver haloids and silver thiocyanate (A., 1908, ii, 378), and points out that Küster and Thiel's investigations (A., 1899, ii, 205; 1900, ii, 255, 521; 1903, ii, 136) had apparently been overlooked. These have shown that in the cases studied by Hill solid solutions are formed, and it therefore follows that his method is inapplicable. E. G.

Relative Solubility of Certain Silver Salts. ARTHUR E. HILL (*J. Amer. Chem. Soc.*, 1915, **37**, 510—513).—A reply to Thiel (preceding abtsract). E. G.

The Equilibrium $BaCO_3,H_2O$. G. WEISSENBERGER (*Zeitsch. physikal. Chem.*, 1914, **88**, 257—270).—The solubility of barium carbonate in water has been determined by the direct gravimetric method at temperatures from 13° to 37°. A critical résumé is given of the methods previously adopted for this determination, and the points of inexactitude noted. The determinations were effected in nickel apparatus, and 2 litres of solution were evaporated in each case. A series of apparent solubilities are thus obtained. A second series are obtained by using water containing small quantities of sodium hydroxide which represses the hydrolysis, and so furnishes a lower and more accurate value for the solubility. The minimum solubility of barium carbonate is found in aqueous solution containing $1{\cdot}25\times10^{-5}$ mols. of sodium hydroxide. The following values are obtained: (1) for pure water at 13°, $1{\cdot}62\times10^{-3}$; 18°, $1{\cdot}72\times10^{-3}$; 22°, $1{\cdot}83\times10^{-3}$; 27°, $1{\cdot}96\times10^{-3}$; 33°, $2{\cdot}14\times10^{-3}$; 37°, $2{\cdot}28\times10^{-3}$ mols. per litre, and (2) the true values calculated from the experimental results obtained in faintly alkaline solution, at 14°, $4{\cdot}32\times10^{-4}$; 18°, $4{\cdot}57\times10^{-4}$; 23°, $4{\cdot}89\times10^{-4}$; 27°, $5{\cdot}22\times10^{-4}$; 32°, $5{\cdot}69\times10^{-4}$; and 38°, $6{\cdot}27\times10^{-4}$ gram-mol. per litre. J. F. S.

Metallic "Fogs." I. Lead Fog in Lead Chloride. RICHARD LORENZ and W. EITEL (*Zeitsch. anorg. Chem.*, 1915, **91**, 46—56. Compare A., 1907, ii, 735; 1911, ii, 379, 491).—Optically clear lead chloride is obtained by fusing the best commercial salt in a glass tube, and passing a stream of dry chlorine and hydrogen chloride through it. Such material does not show the Tyndall effect. By using a glass tube which is approximately rectangular in section, well-developed crystals may be obtained as the mass cools. These crystals have been measured and described. They have D^{17} 5·840, and a mean refractive index between 2·1 and 2·3. By heating 100—150° above the melting point, and adding fragments of lead, the fog is obtained, and after five minutes the mass is allowed to solidify. The crystals obtained by cleavage are still transparent, although very dark. Ultramicroscopical observations show that their constitution is similar to that of ruby glass. The colloidal particles are often grouped parallel to crystalline or cleavage planes, or in crystalline aggregates often at a distance from the boundaries.

The turbid crystals are rendered optically clear by passing chlorine and hydrogen chloride. The slight turbidity of ordinary lead chloride after fusion is due to partial dissociation.

C. H. D.

Metallic "Fogs." II. Silver Fog in Silver Chloride and Bromide. R. LORENZ and W. EITEL (*Zeitsch. anorg. Chem.*, 1915, **91**, 57—60. Compare preceding abstract).—Fused silver chloride is rendered optically clear by passing a stream of dry chlorine, containing a little hydrogen chloride, through the liquid. Silver bromide is stirred with liquid bromine. In both cases clear crystals are obtained, the chloride being colourless and the bromide lemon-yellow. Well-developed crystal faces are absent, but octahedral skeletons are sometimes observed. The crystals are highly plastic.

By adding pure silver at 1000°, the fog is obtained, the crystals being brown on solidification. In the ultramicroscope the particles resemble those of lead, but are not geometrically arranged.

When a mass of clear silver chloride is exposed to bright light it becomes violet, and ultimately black, but remains optically clear.

The turbid crystals are again rendered clear by treatment with chlorine or bromine. C. H. D.

Metallic "Fogs." III. Thallium Fog in Thallium Chloride and Bromide. RICHARD LORENZ and W. EITEL (*Zeitsch. anorg. Chem.*, 1915, **91**, 61—65. Compare preceding abstracts).—Thallous chloride and bromide have not been obtained in an optically clear condition, although the chloride is nearly so when freshly prepared. Both salts are plastic.

The fog may be obtained by adding metallic thallium, or by electrolysing the fused chloride between graphite electrodes.

The colloidal particles resemble those of lead and silver, and are often arranged parallel with the octahedral faces. The particles are very minute, so that green or red colorations are always obtained. Treatment with halogens lessens the turbidity, but results in the formation of double salts. C. H. D.

Hardness of Copper-Zinc Alloys. D. MENEGHINI (*Ann. Chim. Applicata*, 1915, **3**, 95—101. Compare A., 1914, ii, 849).—Recent work on this subject has been carried out by Kurnakov and Shemtschuschni (A., 1908, ii, 932), Guillet and Révillon (*Rev. Métal.*, 1909, **6**, 1251), Andrew (A., 1914, ii, 466), and Turner and Murray (*J. Inst. Metals*, 1909, **2**, 98). The author's measurements were made by a modification of Le Gris' method (*Rev. Métal.*, 1913, **10**, 1058), in which the hardness is calculated from the diameter of the imprint made on the specimen by a steel ball subjected to a relatively small pressure.

With more than 55% of zinc the alloys become hard, brittle, and difficult to work, and with 78—88% of zinc they are porous, and remain so even after re-fusion. From 0% to 50% of zinc the hardness curve is much flatter and less sinuous than was found by Turner and Murray, who observed also great irregularity in the region of about 90% of zinc, probably owing to the difficulty of obtaining perfect equilibrium in the solid phase. Indeed, the author finds that in alloys containing 20—30% of zinc appreciable variation in the hardness may be caused by imperfect re-heating.

Comparison of the hardness curve with that of electrical conductivity, deduced from the data of Haas, Weber, and Matthiessen, gives a further confirmation of Guertler's rule, according to which increased hardness of an alloy corresponds with diminished conductivity (A., 1907, ii, 65). In both the hardness and conductivity curves a change in direction occurs at about 36·5% of zinc, corresponding with the first appearance of the γ-constituent; alloys containing 0—36% of zinc consist exclusively of homogeneous α-solid solutions. The hardness increases very considerably as the proportion of γ-modification becomes greater, and at about 60% of zinc,

where the α-constituent disappears entirely from the solid, it has increased almost fourfold. With the presence of the ϵ-form corresponds the zone of greatest porosity, which ceases with the appearance of the η-constituent. In spite of the coincidence of the maximal hardness with the composition, Cu_2Zn_3, the curve is insufficient to prove the existence of definite compounds, but it confirms the conclusion that 40% of zinc is the maximum permissible in alloys to be utilised industrially. T. H. P.

Mercuric Iodide. I. A. Smits and S. C. Bokhorst (*Zeitsch. physikal. Chem.*, 1915, **89**, 365—373).—It has been shown by Rodwell (*Phil. Trans.*, 1882, **173**, 1125) that when mercuric iodide which has passed into the yellow variety at 128° is further heated, it slowly becomes red again, the colour deepening continuously between 180° and 255·3°. At the higher temperature, it melts to a dark red liquid. The authors have investigated the continuous colour change in connexion with the theory of allotropy. The method consists in heating mercuric iodide to definite temperatures and then suddenly cooling by plunging it into liquid air. The cooled mass is then examined microscopically. It is shown that the continuous change of the yellow variety into the red variety at temperatures above 127°, coupled with the facts (1) that molten mercuric iodide is red, and solidifies to a red solid which cannot be distinguished from the ordinary red variety, (2) that mercury iodide vapour is yellow, and (3) the experimental results, leads to the same Tx diagram for mercuric iodide as has been previously deduced. J. F. S.

Mercuric Iodide. II. A. Smits and S. C. Bokhorst (*Zeitsch. physikal. Chem.*, 1915, **89**, 374—382. Compare preceding abstract).—The fusion curves of the binary systems mercuric iodide–nitrobenzene and mercuric iodide–nitrotoluene have been determined at temperatures up to the melting point of mercuric iodide. The method of determination consisted in accurately weighing quantities of the two components into a cylindrical tube, cooling with liquid air, evacuating and sealing off. The tubes were placed in a thermostat and shaken, and the temperature determined at which the last particles of mercuric iodide passed into solution. This gave the melting point of the given mixture. In the two systems examined the transition point of mercuric iodide is found to be 128° and 127·5° respectively. From the transition point to the melting point the fusion curve is continuous, and between 240° and 250° exhibits an extremely large increase in the value of dx/dt. It is also shown that the colour change above 127° takes place continuously, and that in the region where the colour change is greatest the value of dx/dT of the fusion curve undergoes the greatest change. J. F. S.

Alloys of Mercury with Thallium. P. Pavlovitsch (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 29—46).—The author has investigated the complete melting-point diagram of the system Hg–Tl, the elec-

trical conductivity of the alloys containing 0—40% of thallium, and the hardness, by Brinel's method, of the alloys containing 90—100% of thallium.

Kurnakov and Pushin's supposition concerning the existence in the fusion diagram of an irrational maximum, not corresponding with simple atomic proportions of the constituent atoms, is confirmed; the composition at this maximum is 29—30 at. % of thallium. The curve of conductivity shows a maximum at 26—28 at. % of thallium, and the potential curve a re-entrant angle at 27—28·4 at. % of thallium, both of these being also irrational points. In the absence from these curves of separate or, as Kurnakov styles them, singular or Dalton points, the α-phase in the system Hg–Tl resembles the γ-phase of the system Tl–Bi (compare Kurnakov, Shemtschushni, and Tararin, A., 1913, ii, 410).

This irrationality may be explained by the existence of the dissociating compound, Hg_3Tl, which forms with the components solid solutions within the limits 21—31 at. % of thallium. According to Stepanov's rule, the magnitude of the temperature-coefficient of resistance, which approximates to that for pure metals (0·004), indicates the existence of a chemical compound in the α-phase. Within the limits 86—100° of thallium, the latter forms with mercury β-solid solutions, characterised by enormously increased hardness. T. H. P.

Revision of the Atomic Weight of Praseodymium. Analysis of Praseodymium Chloride. Gregory Paul Baxter and Olus Jesse Stewart (*J. Amer. Chem. Soc.*, 1915, **37**, 516—536).—Baxter and Chapin (A., 1911, ii, 285) have determined the atomic weight of neodymium by purifying the material by the fractional crystallisation of neodymium ammonium nitrate and analysing the chloride. As this method was found satisfactory, it has now been applied to praseodymium.

Ten kilograms of praseodymium ammonium nitrate, containing about 50% of the lanthanum and cerium salts and a small proportion of neodymium, were submitted to a prolonged fractional crystallisation from dilute nitric acid, and the purer fractions were examined spectroscopically. Each fraction of the praseodymium ammonium nitrate used for the determination of the atomic weight was converted into the oxalate by precipitation with oxalic acid, and the oxalate was ignited to oxide; the oxide was dissolved in nitric acid, the oxalate re-precipitated by means of ammonium oxalate, and again ignited. The oxide was dissolved in hydrochloric acid, and the chloride recrystallised three or four times by passing hydrogen chloride into a concentrated solution at 0°. Measurements were made of the absorption spectrum of the praseodymium chloride. In order to remove the last traces of water, the praseodymium chloride was heated until it fused. It was found that the fused chloride sometimes contained a small amount of an insoluble substance in the form of glistening particles which proved to be the oxychloride, PrOCl. The amount of this compound produced increases with the period of fusion, but by

reducing this to less than one minute the quantity produced was less than 1 mg. in 5 grams of the chloride.

Weighed quantities of praseodymium chloride were converted into silver chloride by means of silver nitrate prepared from specially purified silver, and the usual corrections were applied. The final, corrected average of a large number of results gave the value 140·92 for the atomic weight of praseodymium (Ag = 107·880; Cl = 35·457), which approximates closely to the value obtained by Brauner (P., 1898, **14**, 70; 1901, **17**, 65), but is more than 0·3 higher than that adopted by the International Committee on Atomic Weights.

Praseodymium chloride has D^{25} 4·020. E. G.

The Chemical or Physical Nature of the Colloidal Hydrous Aluminium Silicates. Georg Wiegner (*Kolloid. Zeitsch.*, 1914, **15**, 167—169).—A further reply to Gans (A., 1914, ii, 55, 469, 657). H. M. D.

Hydrated Ferric Oxide. Wilder D. Bancroft (*J. Physical Chem.*, 1915, **19**, 232—240).—A paper in which it is shown that any number of hydrated ferric oxide solutions can be obtained which differ in some particular from one another. Ferric oxide prepared by St. Gilles (*Compt. rend.*, 1855, **40**, 568, 1243) is sandy, and contains relatively little water, whilst that prepared by Graham (T., 1862, **15**, 249) is gelatinous and contains more water. The ferric oxide prepared by the latter method is not as homogeneous as that prepared by the former method, because it is always slowly changing into a less hydrated form. The particles of the St. Gilles oxide are coarser (about 7 μ) than the Graham oxide, but their sandy character makes them coalesce less readily, and consequently they are peptonised more readily after precipitation by hydrochloric and nitric acids. The salts and acids which precipitate the St. Gilles oxide readily, precipitate it in a gelatinous form, approximately that of the Graham oxide. The irreversibility of the precipitation seems to be due more to the coalescing of the somewhat gelatinous particles than to the difficulty of washing out the precipitating agent. It is probable, although not proved, that a difference in the physical properties of the precipitated mass may play a part in the irreversibility of precipitation of albumin. The coarse particles of the St. Gilles oxide are less readily attacked by cold acids than are the fine particles of the Graham oxide. A satisfactory theory cannot be advanced for the yellow colour of hydrated limonites. It is not probable that a hydrated hydroxide is being dealt with, and it is not proved that the colour is due to the adsorption of an iron salt, although this is a possible hypothesis. The fact that Fischer (A., 1910, ii, 299, 856) obtained both limonite and hæmatite by heating the Graham ferric oxide with hydrochloric acid is undoubtedly due to the nonhomogeneity of the Graham oxide. J. F. S.

The Asymmetric Cobalt Atom. XII. Optical Activity of Carbon-free Compounds. A. Werner (*Ber.*, 1914, **47**, 3087—3094).—After many unsuccessful searches after purely inor-

ganic compounds which exhibit optical activity, it has been found that the dodecamminehexoltetracobaltihaloids may be resolved by means of the silver bromocamphorsulphonates. It has been shown that these salts have the constitution

$$\{Co[(OH)_2Co(NH_3)_4]_3\}X_6$$

(A., 1907, i, 482; 1914, ii, 787). They therefore belong to the general type $[MA_3]X_n$, of which numerous examples in which A represents a co-ordinate, bivalent radicle, like ethylenediamine, have already been resolved into optical isomerides.

Dodecamminehexoltetracobaltichloride is best prepared by Jörgensen's method from chloroaquotetramminecobalt chloride (A., 1898, ii, 227). This was mixed with sufficient of the silver bromocamphorsulphonate to precipitate all the chlorine, and treated with very dilute acetic acid. The first crops of the *d*-bromocamphorsulphonate crystals were usually lævorotatory, those of the *l*-bromocamphorsulphonate, dextrorotatory. The highest rotation was exhibited by a specimen of well-developed, grey crystals, namely, $[\alpha]_{560}$ −620° in aqueous acetone. The active bromides were prepared by dissolving these salts in just sufficient aqueous acetone (50%), adding small quantities of sodium bromide until the precipitate had a marked activity, and then diluting the mother liquor with absolute alcohol. The *inactive* salt,

$$\{Co(OH)_6[Co(NH_3)_4]_3\}Br_6,8H_2O,$$

was converted into the sulphate (Jörgensen) by precipitation with sodium sulphate, which proved that the constitution of the molecule was the expected one. The d- and l-*bromides* crystallised as reddish-grey powders with $2H_2O$. The salts exhibit most abnormal rotation-dispersion, which will be studied in detail, although the deep colour and rapid racemisation of the solutions render this difficult. The highest rotations observed were $[\alpha]_{560}$ +4446° and −4500° in 50% aqueous acetone, whilst the following values for the *d*-bromide may be taken to illustrate the connexion between rotation and wave-length:

Wave-length	675	643·5	617·5	607·5	560	507·5	495	478
[α]	−670°	−2100°	0°	+1284°	+4446°	+1452°	0°	−858°

J. C. W.

Metal Sols from Carbonyls. Wa. Ostwald (*Kolloid. Zeitsch.*, 1914, **15**, 204).—When a colourless solution of nickel carbonyl in benzene is boiled, carbon monoxide is evolved, and a violet-grey colloidal solution of nickel remains. On keeping for twelve hours the metal is partly coagulated. If prepared at a lower temperature the colloidal solution is more stable. The nickel can be removed by shaking with hydrochloric acid.

A benzene solution of nickel carbonyl deposits nickel hydroxide on keeping for some days.

It is proposed to extend the above method to other solvents so as to ascertain the influence of this, and of the temperature of decomposition on the degree of dispersity of the colloidal metal.

H. M. D.

The Transformations of Chromium and Titanium Trichlorides in Aqueous Solution. ADOLF HEYDWEILLER (*Zeitsch. anorg. Chem.*, 1915, **91**, 66—74. Compare Roozeboom and Olie, A., 1905, ii, 716).—The density and electrical conductivity of dilute solutions prepared from the first green chromium trichloride hexahydrate have been determined. A rapid change to the second green salt takes place, followed by a second slow transformation into the violet salt, the latter reaction giving a very regular constant. The figures obtained correspond with a bimolecular reaction with a large excess of one component, indicating a reaction between the non-ionised molecules and water, ions being first separated and then hydrated. The tribromide undergoes very rapid transformation.

A violet solution of titanium trichloride hexahydrate increases in conductivity until the value is nearly doubled. The density remains almost unchanged, but the colour becomes much lighter. The velocity of reaction increases very rapidly with increasing dilution. The results are less regular than with chromium, and indicate the formation of an oxychloride by absorption of oxygen. Hydrolysis also occurs. C. H. D.

Iso- and Hetero-poly-acids. XI. Unsaturated Molybdoarsenates and -phosphates. ARTHUR ROSENHEIM and ADELE TRAUBE (*Zeitsch. anorg. Chem.*, 1915, **91**, 75—106).—Heteropoly-salts belong to the limiting series when their anions have the highest possible basicity. They are further distinguished as "saturated" when the whole of the oxygen atoms of the parent anion are replaced by metallic acid anions, and as "unsaturated" when only part are replaced. The passage from saturated to unsaturated salts may take place through hydrolysis.

Several deductions from Werner and Miolati's hypothesis are made, and tested by their application to unsaturated hetero-poly-salts.

3-Molybdoarsenates are salts of a tribasic acid,

$$H_3\left[As\begin{matrix}(MoO_4)_3\\ O\end{matrix}\right].$$

The complex anion of this series is the most stable of those derived from $[XO_4]$. The 9-molybdoarsenates are salts of a hexabasic acid:

$$H_6\left[\begin{matrix}As\\ O\end{matrix}\begin{matrix}(Mo_2O_7)_4\\ \diagdown\end{matrix}\begin{matrix}(Mo_2O_7)_4\\ \diagup\end{matrix}\begin{matrix}As\\ O\end{matrix}\right]H_6.$$
$$\qquad\qquad -Mo_2O_7-$$

The corresponding 9-molybdophosphates are converted by further hydrolysis into 17-molybdo-2-phosphates.

3-Molybdoarsenic acid, $H_3\left[As\begin{matrix}(MoO_4)_3\\ O\end{matrix}\right],6{\cdot}5H_2O$, is obtained by saturating a solution of arsenic acid with molybdenum trioxide, evaporating to a syrup, cooling with ice, and adding fuming nitric acid. White crystals separate, which may be recrystallised from water. It is a tribasic acid, stronger than arsenic acid. The *trisodium* salt crystallises from water with $11{\cdot}5H_2O$, and the triguanidinium salt forms pale yellow, anhydrous needles. Other salts have been described by Pufahl (A., 1884, 715).

The sodium salt of 9-molybdoarsenic acid is yellow with $20H_2O$, and colourless with $25H_2O$. A difference of constitution must exist, but has not been explained. The yellow solution gives with cæsium chloride a colourless precipitate of the salt:

$$Cs_{12}\left[As_2^{(Mo_2O_7)_9}_{O_2}\right],5H_2O.$$

9-Molybdophosphoric acid crystallises with $30H_2O$ in orange prisms, which in contact with the solution gradually take up a further $4H_2O$, forming yellow crystals. The conductivity indicates a basicity higher than six, and the salt

$$Na_6H_6\left[P_2^{(Mo_2O_7)_9}_{O_4}\right],28H_2O$$

behaves as an acid salt. It is yellow, and changes into a colourless salt with $38H_2O$. The *guanidinium* salt,

$$(CN_3H_6)_{12}\left[P_2^{(Mo_2O_7)_9}_{O_2}\right],30H_2O,$$

and the *silver* salt, $Ag_{12}\left[P_2^{(Mo_2O_7)_9}_{O_3}\right],20H_2O$, prove the basicity to be 12.

The sodium salt yields with potassium chloride and potassium hydrogen carbonate a colourless salt, $K_{10}Na_6\left[P_4^{(Mo_2O_7)_{17}}_{O_4}\right],36H_2O$, whilst the corresponding ammonium sodium salt contains $33H_2O$. The guanidinium and silver salts (Ag_{22}, etc.) each contain $40H_2O$.

C. H. D.

Optical Investigation of the Precipitation of Tungstic Acid from Sodium Tungstate Solutions by Acids. A. Lottermoser (*Kolloid. Zeitsch.*, 1914, **15**, 145—149).—The precipitation of tungstic acid from dilute solutions of sodium tungstate on the addition of mineral acids takes place gradually, and the process has been followed by measuring the intensity of the light which is transmitted by the solution in terms of the intensity of the incident beam by means of a photo-electric potassium cell. The curves obtained by plotting the relation intensity of the transmitted light indicate that the precipitation is an auto-catalytic process. The velocity is primarily determined by the hydrogen-ion concentration, for it is found that the change takes place more rapidly with hydrochloric than with sulphuric acid, whilst no precipitation occurs on the addition of acetic acid even when the solution is considerably more concentrated.

H. M. D.

The Controversy Regarding the Existence of Bismuth Suboxide. F. Treubert and L. Vanino (*Zeitsch. anal. Chem.*, 1914, **53**, 564—568).—The authors discuss the various claims put forward as to the existence of bismuth suboxide, its method of preparation and properties (compare A., 1907, ii, 274), and come to the general conclusion that the existence of bismuth suboxide and its salts is disproved.

W. P. S.

The Influence of Foreign Substances in the Preparation of Colloidal Gold Solutions by Zsigmondy's Formaldehyde Method. KARL HIEGE (*Zeitsch. anorg. Chem.*, 1915, **91**, 145—185).—Colloids may hinder the formation of gold nuclei in the reduction process in either of two ways: by uniting with the gold particles, or by means of their electrical charge. To the first class of reagents belong gelatin, sodium protalbate, soaps, stannic acid, and silicic acid which has been "aged," and probably contains traces of organic matter derived from the dialysing membrane. These substances lessen the number of nuclei. All of them belong to the class of protective colloids, and their effect reaches a maximum at a certain concentration. Thus, small additions of gelatin produce dark and turbid solutions, whilst larger additions, after the maximum turbidity has been passed, again become clear and bright red. This is shown by the ultramicroscope to correspond with a change in the number of gold particles, which passes through a minimum. Starch, gum arabic, and freshly prepared silicic acid exert a favourable influence on the formation of nuclei. High concentrations of gelatin, soaps, and sodium protalbate, and the presence of traces of oils, fats, or colloidal sulphur retard the appearance of the nuclei. The results are expressed in tabular form.

The second group is represented by colloidal ferric hydroxide, which carries a positive charge. Small quantities exert a favourable influence, but a very small increase causes coagulation.

The concentration of various electrolytes necessary to cause coagulation has also been determined. Ammonium chloride diminishes the number of gold nuclei, and retards the reduction. Potassium ferro- or ferri-cyanide has a still more pronounced effect. Potassium chloride, bromide, and iodide in small concentrations increase the number of nuclei, but diminish it in higher concentrations. Potassium thiocyanate and oxalate and a few organic salts behave as reducing agents, and give rise to gold nuclei even before the addition of formaldehyde. Observations with some other inorganic salts are also recorded. C. H. D.

New Investigations on the Black Sand of Madagascar and the Platiniferous Minerals of Westphalia. A. DUPARC, A. DEL CAMPO Y CERDAN, and S. PIÑA DE RUBIES (*Anal. Fis. Quim.*, 1915, **13**, 82—88).—The proportion of platinum in the samples of black sand from Madagascar and the Westphalian minerals examined is too small for profitable extraction. A. J. W.

Palladium and Hydrogen. II. ADOLF SIEVERTS (*Zeitsch. physikal. Chem.*, 1914, **88**, 451—478. Compare A., 1914, ii, 626).—A further series of experiments on the adsorption of hydrogen by palladium have been carried out using the same palladium and the same apparatus as previously employed (*loc. cit.*). The relationship between the quantity of hydrogen absorbed and the partial pressure has been obtained at temperatures from 138° to 821° and hydrogen pressures between 1 and 760 mm. It is shown that with

both commercial and pure palladium wire, between the temperature limits mentioned, the quantity of hydrogen absorbed, L_p, by unit weight of palladium is almost proportional to the square root of the hydrogen pressure p. The expression $L_p = kp^{\frac{1}{2}}$ is, however, not strictly followed, for the value $L_p/p^{\frac{1}{2}}$ increases regularly with increasing pressure. The more exact determinations show that the experimental results are better expressed by the equation $L_p = k_1 p^{\frac{1}{2}} + k_2 p$, in which k_1 and k_2 are constants depending on the temperature. This expression can be regarded as representing that the hydrogen molecules are in equilibrium with hydrogen atoms, both in solution in the palladium and in the gas phase, and that Henry's law holds strictly for both atoms and molecules. The dissociation constant of hydrogen has been calculated, and shown to be practically the same at 300° and 820°, but distinctly smaller at 138°, the values of the dissociation constant being: at 138°, 25; 315°, 109; 619°, 112; and 821°, 102. It is shown that the equation is not true for higher pressures, and that it does not offer an explanation of the peculiar isothermals of Troost and Hautefeuille (this Journ., 1874, 660) and Hoitsema (A., 1895, ii, 383). The quantity of hydrogen absorbed by unit weight of palladium depends only on the pressure and temperature, and is entirely independent of the surface area of the metal. Consequently, the absorption of hydrogen by palladium is to be regarded as a true solution phenomenon. The isothermals of palladium-black and palladium-sponge are similar to those of compact palladium, but the actual curves are different with different specimens, and are apparently dependent on the nature of the palladium. With small pressures and concentrations the quantity absorbed is approximately proportional to the square root of the pressure. This approximate relationship also holds good when the activity of palladium-black has been reduced by ignition. The similarity of the absorption isothermals in all cases allows of the conclusion being drawn that in palladium-black and palladium-sponge the absorption is mainly due to solution of the hydrogen, at least at temperatures above 100°. At lower temperatures it is, however, likely that surface adsorption accounts for a large portion of the hydrogen taken up. The above results are in strict accord with the statement (*loc. cit.*) that palladium-black and palladium-sponge are made up of varying quantities of amorphous and crystalline palladium. Both modifications appear to act as solvents for hydrogen with different powers of solution. The fact that the relationship between absorption, pressure, and temperature is similar in all cases is in accord with the above-mentioned statements. The absorption isobars and isothermals of the system palladium–hydrogen give no confirmation of an enantiomorphic transition of palladium in the region of 150°. J. F. S.

Mineralogical Chemistry.

Gases Enclosed in the Lower Silesian Coal Seams. JULIUS MEYER (*J. pr. Chem.*, 1914, [ii], **90**, 141—167).—Analyses have been made of the gases which issue, sometimes with explosive violence, from the coal seams in certain Lower Silesian mines, and they were all found to be characterised by a high carbon dioxide content, over 50% in one case being observed. Analyses of the gases enclosed in the coal of the particular mines subject to these disruptive outbreaks revealed likewise an abnormally high percentage of carbon dioxide, from 48 to 67%, as against a normal quantity of 10—15% found in the coal obtained from other galleries or mines where no outbreaks had been known to occur. The origin of these isolated and highly dangerous accumulations of carbon dioxide, under pressures estimated to be in some cases more than 20 atm., is discussed, and the author favours the view that the gas is produced by the action of superheated water on coal at high pressures, or is the result of a still incomplete coal formation at greater depths according to a reaction of the nature:

$$4C_6H_{10}O_5 = C_{21}H_{16}O_2 + 3CO_2 + 12H_2O.$$

G. F. M.

A Unique Geophysical Phenomenon, Trinidad Asphalt, Interesting from the Point of View of Dispersoid Chemistry. CLIFFORD RICHARDSON (*J. Physical Chem.*, 1915, **19**, 241—249).—A number of analyses of Trinidad asphalt have been carried out. It is shown that the composition is uniform throughout the entire deposit. The aqueous extract contains about 20 grams of salts per litre, consisting of sodium chloride, sodium sulphate, ferrous sulphate, ammonium sulphate, and small quantities of iodides and borates. The general analysis of the material is water and gases (carbon dioxide and hydrogen sulphide), 29·0%; bitumen soluble in cold carbon disulphide, 39·0%; bitumen adsorbed and retained by the disperse mineral matter, 0·3%; mineral matter, 27·2%; water of hydration of clay, 4·2%. The mineral matter consists of fine silica and clay, and the salts mentioned above. The crude asphalt is shown to consist of a suspension of relatively large size particles of mineral matter in an extremely viscous medium, together with highly disperse mineral matter in colloid form, intimately mixed with an emulsion of a thermal water and bitumen.

J. F. S.

The Ternary Fluophosphates Morinite, Ježekite, and Lacroixite. F. SLAVÍK (*Bull. Soc. franç. Min.*, 1914, **37**, 152—162).—The new species ježekite and lacroixite occur, together with other phosphates (childrenite, apatite, and roscherite *) in drusy cavities

* Roscherite is another new species described by F. Slavík in 1914. It is monoclinic and has the composition $(Mn,Fe,Ca)_2Al(OH)P_2O_8,2H_2O$.

in lithionite-granite at Greifenstein, near Ehrenfriedersdorf, in Saxony. Ježekite forms colourless to white, monoclinic crystals ($a:b:c=0{\cdot}8959:1:1{\cdot}0241$; $\beta=74°28\frac{1}{2}'$). Analysis I, by E. Skarnitzl, corresponds with $Al_2O_3,CaO,(NaF)_2,(NaOH)_2,P_2O_5$ or $Na_4CaAl(AlO)P_2O_8F_2(OH)_2$. The mineral thus resembles morinite (A., 1909, ii, 58) in being a basic fluorophosphate of aluminium, calcium, and sodium, but the ratios are somewhat different. The optical and other physical properties are, however, practically identical, and the suggestion is made that the crystals determined by Lacroix as morinite from Montebras, in France, were really acicular crystals of ježekite emplanted on the pink lamellar masses of morinite.

	P_2O_5.	Al_2O_3.	Fe_2O_3.	CaO.	Na.	Li.	F.	OH.	Total.	Sp. gr.
I.	30·30	21·92	trace	13·50	18·71	0·86	8·15	7·26	100·70	2·94

Lacroixite is present as indistinct crystals with an orthorhombic habit and resembling herderite in appearance; the cleavages and optical characters, however, suggest monoclinic symmetry. Anal. II, by A. Jilek, gives the formula:

$$3AlPO_4,4(Ca,Mn)O,4Na(F,OH),2H_2O;$$

traces of iron, magnesium, and lithium are also present:

	P_2O_5.	Al_2O_3.	MnO.	CaO.	NaF.	NaOH.	H_2O.	Total.	Sp. gr.
II.	28·95	18·92	8·45	19·51	14·47	5·51	4·22	100·03	3·126

L. J. S.

Hewettite, Metahewettite, and Pascoite, Hydrous Calcium Vanadates. W. F. Hillebrand, H. E. Merwin, and Fred. E. Wright (*Proc. Amer. Phil. Soc.*, 1914, **53**, 31—54).—The new species hewettite occurs as an alteration product of patronite (A., 1907, ii, 788; 1910, ii, 719) at Minasragra, Peru. It is mahogany-red with a somewhat silky lustre, and under the microscope is seen to consist of minute, orthorhombic needles. D 2·554. The mineral fuses readily to a dark red liquid, and it is slightly soluble in water. Analysis I of material, which was in equilibrium with a water-vapour tension of 21·8 mm. at 25°, gives the formula $CaO,3V_2O_5,9H_2O$, or, written as a hydrated acid hexavanadate, $CaH_2V_6O_{17},8H_2O$. Hewettite has also been identified in a single specimen from Paradox Valley, in Montrose Co., Colorado.

Metahewettite is identical with hewettite in composition, and also resembles it very closely in general characters. It occurs as an impregnation in sandstone at Paradox Valley in Colorado, and over a wide area in Eastern Utah. It is dark red and earthy, and under the microscope shows minute, orthorhombic plates. D 2·511 (2·942 for material with $3H_2O$). Analysis II is of material from Thompson's, Utah, which was in equilibrium with a water-vapour tension of 38·8 mm. at 35°. Associated with this mineral in the sandstone is a grey hydrated silicate of aluminium, tervalent vanadium, and potassium. Embedded in the latter are specks of native selenium, the existence of which as a mineral species has hitherto been doubtful.

Hewettite and metahewettite are extremely sensitive to atmo-

spheric changes in humidity, and nearly all the water can be expelled without breaking down the crystal structure. The analyses were made on material which had been kept over sulphuric acid (D^{15} 1·105). Dehydration curves show a difference in behaviour of the two minerals:

	V_2O_5.	MoO_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Fe_2O_3, etc.	Total.
I.	68·19	1·56	7·38	nil	nil	0·15	21·33	0·11	100·10*
II.	70·01	0·13	7·25	0·03	0·09	0·08	21·30	0·19	100·23†
III.	64·6	0·3	12·6	—	—	—	21·6‡	—	99·1

* Including V_2O_4, 1·21; insoluble, 0·17.
† Including V_2O_3, 0·35; SiO_2 and insoluble, 0·80.
‡ H_2O −100°, 13·8; H_2O +100°, 7·8.

Pascoite occurs as an orange-red or orange-yellow, powdery efflorescence on the walls of the mine workings at Minasragra, Cerro de Pasco. The optical characters of the grains indicate monoclinic symmetry. D 2·457. The mineral melts readily to a dark red liquid, and it is readily soluble in water. Analysis III gives the formula $Ca_2V_6O_{17},11(?)H_2O$. L. J. S.

Wolframite, Beraunite, and Axinite. EDGAR T. WHERRY (*Proc. U.S. National Museum*, 1914, **47**, 501—511). Analysis I is of long-bladed crystals of wolframite from Cornwall, associated with chalcopyrite and quartz; and II of black wolframite from Cave Creek, north of Phœnix, Arizona, where the mineral is associated with chrysocolla, microcline, and quartz. The tantalum and columbium oxides probably exist as the tantalite ($[Fe,Mn]Ta_2O_6$) and columbite ($[Fe,Mn]Cb_2O_6$) molecules in the mixed crystals. No. 1 is described as a ferromanganowolframite, and II as a doferrowolframite:

	FeO.	MnO.	CaO.	MgO.	CuO.	WO_3.
I.	10·81	12·55	0·80	0·12	—	74·84
II.	18·18	3·37	0·24	—	1·34	73·74

	Ta_2O_5.	Cb_2O_5.	SiO_2.	Fe_2O_3.	Total.	Sp. gr.
I.	0·26		0·30	0·70	100·38	7·272
II.	1·50	0·70	0·72	—	99·79	7·162

A ferric phosphate referred to beraunite occurs as a dark brown, nodular crust on quartzite in an iron mine near Hellertown, Northampton Co., Pennsylvania. It is coarsely fibrous, and the D (2·85—2·92) and optical characters agree with those of beraunite. The following analyses (III by J. S. Long, IV by L. H. Koch, and V the mean of two analyses by Wherry) give ratios for $R_2O_3:P_2O_5$ varying between 1·72:1 and 1·93:1, being in excess of the beraunite ratio, 1·5:1, and approaching the dufrenite ratio 2:1. The mineral may thus be a mixture of these, and the name dufreniberaunite is suggested:

	Fe_2O_3.	Mn_2O_3.	P_2O_5.	H_2O.	SiO_2.	Total.
III.	42·91	15·25	28·10	10·01	4·02	100·29
IV.	52·65	3·88	29·27	13·59	0·71	100·10
V.	56·70	1·73	27·98	13·07	0·48	99·96

Axinite occurs in pegmatite at Avondale, Delaware Co., Pennsylvania. Analysis of yellow, platy material, D 3·25, gave VI, by J. E. Whitfield; another determination of boric oxide gave 6·04 by Wherry. Zoisite is sometimes intermixed with this axinite, imparting to it a columnar structure and a pink colour; analyses are also given of the mixture:

	SiO_2.	B_2O_3.	Al_2O_3.	FeO.	MnO.	CaO.	MgO.	H_2O.	Total.
VI.	42·24	3·14	18·78	3·80	10·12	19·98	1·01	0·57	99·64

L. J. S.

Thorianite from Madagascar. A. Lacroix (*Bull. Soc. franç. Min.*, 1914, **37**, 176—180).—Two isolated crystals of thorianite from the province of Betroka in the south of Madagascar are described, but unfortunately no information is available as to the exact locality and mode of occurrence. The larger crystal measures 2½—3 cm. along the edge of the cube, and the smaller is an interpenetration twin with rotation about a triad axis; the forms present are (100), (111), and (311). The colour is brownish-black, and in thin slices brownish-red. The mineral is isotropic, and has a high refractive index. Hardness 6½; D 9·33; strongly radioactive. It is infusible before the blowpipe, and is attacked by concentrated nitric acid. A preliminary analysis by Pisani shows more thorium and less uranium than the original thorianite from Ceylon:

ThO_2.	UO_2.	Fe_2O_3.	PbO.	Total.
93·02	4·73	0·29	1·80	99·84

From the same province large crystals of zircon, sphene, and apatite are recorded. The sphene is brown in colour, and gave on analysis by Pisani:

SiO_2.	TiO_2.	Al_2O_3,	Ce_2O_3.	FeO.	CaO.	Loss on ignition.	Total.
31·00	35·40	4·00	0·40	1·60	27·20	0·66	100·26

L. J. S.

The Constitution of the Natural Silicates. Frank W. Clarke (*Bull. U.S. Geol. Survey*, 1914, **588**, 1—128).—A new edition of Bulletin No. 125 (A., 1897, ii, 50). L. J. S.

Actinolite from Algeria. Azéma (*Bull. Soc. franç. Min.*, 1914, **37**, 124—129).—Various mineral specimens are described. Clear, green actinolite from Ain-el-Ouarka (South Oranais) gave on analysis:

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.	Na_2O.	K_2O.	H_2O.	Total.
54·52	1·32	2·16	9·93	0·25	17·70	12·43	0·66	0·22	0·93	100·12

corresponding with $16[(Ca,Mg,Fe)O,SiO_2]+1[Na_2O,Al_2O_3,4SiO_2]$.

L. J. S.

Opal and a New Mineral (Faratsihite) from Faratsiho, Madagascar. A. Lacroix (*Bull. Soc. franç. Min.*, 1914, [*i.e.*, 1915], **37**, 231—236).—Altered phonolitic trachyte in the neighbourhood

of Faratsiho, near Ankaratra, contains veins and pockets of opal. This is usually white and opaque (cacholong), but the gem varieties (precious opal and fire-opal) also occur. Sometimes in the upper layers the material is gelatinous and cheesy, drying on exposure to a soft, porous mass. Associated with this opal is the canary-yellow mineral faratsihite, forming ropy masses with smooth, rounded surfaces. It is compact and sectile, and adheres to the tongue; D slightly over 2. It is decomposed by hydrochloric acid with the separation of pulverulent silica; and very thin splinters are fusible before the blowpipe to a grey glass. The fracture is finely granular; and under the microscope are seen minute, hexagonal plates, usually grouped in piles as in kaolinite. The following analysis by RAOULT gives the ratios $SiO_2:(Al,Fe)_2O_3:H_2O = 2\cdot2:1:2\cdot3$, or approximately $2SiO_2,(Al,Fe)_2O_3,2H_2O$:

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.
41·60	22·68	15·22	0·54	0·11	0·60	0·16

K_2O.	TiO_2.	P_2O_5.	H_2O at 105°.	H_2O ignition.	Total.
0·22	0·13	0·21	5·71	13·02	100·20

The water given off at 105° does not enter into the constitution of the mineral, and several of the constituents present in small amount are regarded as admixed impurities. The mineral is thus intermediate in composition between kaolinite (which it resembles in structure) and nontronite (which it resembles in colour), but since kaolinite never contains iron and nontronite is generally poor in aluminium, the present mineral is regarded as a distinct species, and accordingly named faratishite.. L. J. S.

Garnets of the Almandine–Spessartite–Pyrope Groups from Madagascar. A. LACROIX (*Bull. Soc. franç. Min.*, 1914, **37**, 108—112).—In Madagascar, garnets, sometimes of gem quality, occur in pegmatites and in crystalline schists, those of the almandine-spessartite group in the former, and those of the almandine-pyrope group in the latter rocks. The pegmatites are of two kinds, potassic and sodic, the former with a predominance of microcline and muscovite, and the latter with abundance of albite, together with associated lithium minerals (lepidolite, rubellite, etc.). The garnets of the sodic pegmatites are, as a rule, paler in colour (brownish-red to orange) than those of the potassic pegmatites. A nearly pure spessartite and one with more iron have been described by Duparc (A., 1910, ii, 221; 1914, ii, 664), and another member of this group, now analysed by Pisani (anal. I), contains still more iron, being intermediate between almandine and spessartite:

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO·	MgO.	CaO.	Loss on ignition.	Total.	Sp. gr.
I.	35·40	19·35	1·80	20·20	22·80	1·02	—	—	100·57	4·17
II.	38·70	21·81	—	23·75	1·86	9·21	5·34	—	100·67	3·95
III.	38·80	24·30	—	18·80	0·85	10·82	5·93	—	99·51	3·82
IV.	38·6	19·1	5·5	20·6	0·7	10·9	4·6	—	100·00	3·82
V.	41·10	22·40	—	23·40	0·44	11·12	1·92	—	100·38	3·80
VI.	39·90	22·80	—	17·50	0·80	14·70	3·75	0·20	99·65	3·75

Analyses II—VI, by Pisani, are of garnets intermediate between almandine and pyrope; II, dark blood-red, from near Benenitra; III, dark blood-red in amphibolite, from the river Sakatovo; IV, clear, rose-red in leptynite, from near Ampanihy (the composition as given is calculated from the analysis of the rock); V, dark blood-red in manjakite from Volotara; VI, clear, rose-red from Ianapera. The last of these approaches rhodolite in composition.

L. J. S.

The Analcite-Basalts of Sardinia. H. S. WASHINGTON (*J. Geol.* 1914, **22**, 742—753; *Boll. Soc. Geol. Italiana*, 1914, **33**, 147—167). —Certain rocks from the lava flows of Monte Ferru and Bonorva in Sardinia, which have hitherto been described as leucite-basalts, show on analysis an excess of sodium (Na_2O, 3·67—5·11%) over potassium (K_2O, 0·72—1·64). Warm dilute hydrochloric acid extracts from the rock Na_2O 2·66% and K_2O 0·12%. The isotropic crystals previously regarded as leucite are thus proved to be analcite. They show zonally arranged enclosures, but there is an entire absence of lamellar twinning and optical anomalies. The analcite is an original constituent of the rock. The rock from a flow near Scano on Monte Ferru contains an abundance of nodules of olivine and augite. The olivine nodules, D^{20} 3·307 (anal. I), consist of an aggregate of small grains, whilst those of augite (anal. II) consist each of a single crystal. The analcite-basalt from Ghizo contains much copper-red biotite, and this rock type is called ghizite.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	NiO.
I.	41·24	0·10	0·21	0·48	8·36	trace	0·21
II.	50·13	1·91	7·08	1·10	4·41	0·05	0·02

	MgO.	CaO.	Na_2O.	K_2O.	H_2O.	Total.
I.	49·90	nil	—	—	—	100·62
II.	13·73	20·06	1·88	0·25	0·11	100·73

L. J. S.

Analytical Chemistry.

Fluorescence in Microchemical Analysis. W. Lenz (*Zeitsch. anal. Chem.*, 1915, **45**, 27—42).—Using a fluore cence microscope, the arrangement of which is described, the author has investigated eighty-seven different substances in ultra-violet light, and finds that thirty-one of them fluoresce. Six of them, namely, ammonium and potassium platinichlorides, cobalt mercurithiocyanate, mercuric iodide, silver iodide, and nickel dicyanodiamidine, fluoresce with practically their own colour, and thus tend to contradict Stokes' rule. Four compounds, namely, benzidine chromate, hydrochloride and sulphate, and nitron nitrate, owe their fluorescence to

the organic part of the molecule. Of the remaining twenty-four compounds, it is probable that their fluorescence may form a useful test in the case of the following: arsenic trioxide, sodium uranyl-acetate, sodium pyroantimonate, silver and mercurous haloids.

T. S. P.

Modified Jannasch's Bromine Apparatus. VIKTOR ZSIVNY (*Zeitsch. anal. Chem.*, 1915, **54**, 159—161).—In the absorption apparatus described for use in Jannasch's method for the analysis of ores (heating in a current of carbon dioxide charged with bromine vapour; compare A., 1906, ii, 394) all the connexions between the vessels should be made by ground-in joints. Such an apparatus, consisting of a globular receiver and three absorption flasks, is described. W. P. S.

Weighing Pipette. A. T. MERTES (*J. Ind. Eng. Chem.*, 1915, **7**, 236).—A weighing pipette for use with glycerol, oils, etc., consists of a small pipette provided with a tap on its stem and having its upper end bent into the shape of a hook by which it may be suspended on the balance. W. P. S.

Filter-Pipette for Ether. J. M. PICKEL (*J. Ind. Eng. Chem.*, 1915, **7**, 236—237).—The ether is contained in a bottle closed with a cork, through which pass two tubes; one of these extends nearly to the bottom of the bottle, and is surrounded by a wider tube, to the lower end of which an ordinary paper filter thimble is attached. The upper end of this tube is bent downwards, and passes through a cork into a small pipette provided with a siphon arrangement. A rubber ball fitted with one valve is attached to the outer end of the other tube, the ball having a small hole in its side; a finger is placed over this hole while the ball is compressed to force the ether inwards through the filter thimble and thence into the pipette, the finger being removed as soon as the pipette is full and the siphon commences to deliver the ether. The capacity of the pipette may be such that any desired quantity of ether may be discharged each time the pipette is filled up to the level at which the siphon operates. W. P. S.

Ether Recovery Tube. J. M. PICKEL (*J. Ind. Eng. Chem.*, 1915, **7**, 236).—In fat extractions with the use of a Knorr flask, a glass device is placed in the part of the apparatus above the extraction tube; during the extraction, one-half of this device acts as a funnel and conducts the ether from the reflux apparatus to the extraction tube. The other half of the device consists of a tube which, when the extraction is completed, is brought under the end of the reflux apparatus so as to collect the ether. W. P. S.

Titration of Chlorine Ions in Natural Waters. OTTO MAYER (*Zeitsch. anal. Chem.*, 1915, **54**, 147—158. Compare A., 1914, ii, 573).—Titration with standard silver nitrate solution yields approximately accurate results, whether a small or large quantity of

potassium chromate solution is used as the indicator; with large quantities of the indicator, the colour change appears sooner than with small quantities. In all cases comparison solutions should be employed for detecting the point at which the colour of the indicator changes. The volumetric method is sufficiently trustworthy for use in water analysis, but when accurate estimations of chlorine ions have to be made, the gravimetric method should be used.

W. P. S.

Estimation of Dissolved Oxygen in Water. L. W. WINKLER (*Zeitsch. anal. Chem.*, 1914, **53**, 665—672).—The following modification of the author's well-known method is described for the estimation of dissolved oxygen in waters containing both nitrites and organic substances having an interfering action on the process. A bottle is filled with the water in question, manganous chloride solution and sodium hydroxide solution free from potassium iodide are added in the usual way, and a current of carbon dioxide is then passed into the water. The manganous hydroxide is thus converted into manganous carbonate and manganous hydrogen carbonate; about ten minutes' treatment with carbon dioxide is sufficient. The precipitate is collected on a filter, washed with a 2% potassium hydrogen carbonate solution, dissolved in dilute hydrochloric acid containing potassium iodide, and the liberated iodine titrated. The manganous carbonate is not oxidised by atmospheric oxygen during the filtration. W. P. S.

Method of Valuing Hyposulphites. EDMUND KNECHT (*J. Soc. Dyers*, 1915, **31**, 94—96).—Whilst sulphites are without action on chromates in alkaline solution, hyposulphites are oxidised to sulphites, the chromate being reduced and a corresponding quantity of chromium hydroxide precipitated. The reaction proceeds according to the equation:

$$2Na_2CrO_4 + 3Na_2S_2O_4 + 2NaOH = 6Na_2SO_3 + Cr_2O_3 + H_2O.$$

A weighed quantity of about 0·2 gram of the hyposulphite under examination is introduced in the dry state into a flask containing 20 c.c. of approximately $N/10$-dichromate solution previously rendered alkaline with sodium hydroxide. The mixture is boiled for five minutes, the chromium hydroxide collected on a filter, and washed; the filter and precipitate are then boiled with water to which sodium peroxide is added, the excess of sodium peroxide is decomposed by continuing the boiling for a short time, and the resulting chromate is titrated with titanous chloride solution after the solution has been acidified with sulphuric acid. W. P. S.

Estimation of Ammonia in Soils. R. S. POTTER and R. S. SNYDER (*J. Ind. Eng. Chem.*, 1915, **7**, 221—226).—Folin's aëration method (A., 1913, ii, 239) was found to be the most trustworthy for this purpose; in the dilution at which soil solutions are examined there is no precipitation of ammonium magnesium phosphate and consequent retention of ammonia. The ammonia should be liberated by means of sodium carbonate; when sodium

hydroxide is employed, as recommended by Steele (A., 1911, ii, 68), the results obtained are too high, owing chiefly to the decomposition of acid amides, particularly acetamide; sodium carbonate does not bring about this decomposition. The aeration method gives lower results than those obtained by direct distillation with magnesia, the difference being due to partial decomposition of organic substances by magnesia; the amount of ammonia obtained by the latter method depends on the duration of the distillation. The amount of ammonia extracted by hydrochloric acid from soils varies from 60 to 70% of the quantity present, and is independent of the strength of the acid and the period of extraction.

W. P. S.

Importance of the Occurrence of Nitrates in Milk and their Detection. E. FRITZMANN (*Bied. Zentr.*, 1914, **43**, 647; from *Molk. Zeit.*, 1914, **28**, 663).—For the examination of milk for nitrates (as indicating the presence of added water) a solution of formaldehyde in sulphuric acid (D 1·82—1·825) is employed. A blue coloration is, however, not necessarily due to the presence of nitrates, and may be produced by preservatives such as dichromate, hydrogen peroxide, and ferric salts, so that the process is only of use where no preservatives have been employed. N. H. J. M.

Estimation of Phosphoric Acid in Soil Extracts. L. G. DEN BERGER (*Bied. Zentr.*, 1914, **43**, 670—671; from *Intern. Mitt. Bodenk.*, 1914, **4**, 46).—The following method is employed for soils containing titanium: An aliquot portion of the hydrochloric acid extract is diluted, boiled, and treated with a slight excess of ammonia. The precipitate is washed twice with hot water, dried on the filter, ignited in a platinum crucible, and fused with 2—4 parts of anhydrous sodium carbonate. It is then extracted with cold water, filtered, and washed until 20 drops of the filtrate give no residue when evaporated. The residue contains ferric oxide, and all the titanium in the form of sodium hydrogen titanate. The filtrate, which may be turbid owing to ferric oxide passing through, is acidified with nitric acid until the alumina at first precipitated redissolves, evaporated down, and the phosphoric acid estimated in the usual manner. N. H. J. M.

Iodometric Estimation of Phosphoric Acid in Vegetable Products and Soils. J. PREISINGER and FR. FRODL (*Bied. Zentr.*, 1914, **43**, 608—609; from *Zeits. landw. Versuchswesen Oesterr.*, 1914, **17**, 92).—The substance (10—20 grams of hay or straw, etc.) is left overnight with fuming nitric acid (20—25 c.c.), and then heated with strong sulphuric acid (10—15 c.c.) until all the brown fumes are expelled. Nitric acid is then added until the solution is colourless, or slightly yellow. The solution is diluted to 200 c.c., and after the silica has settled, 20—25 c.c. are taken out and diluted to 40—50 c.c. with nitric acid, sulphuric acid, and water, so as to contain 1—1·5 c.c. of strong sulphuric acid and 10 c.c. of strong nitric acid, and precipitated by Lorenz's method.

The precipitate is left, according to the amount, for two to eighteen hours, filtered, and washed with tap-water until free from sulphuric acid, and is then, along with the filter, transferred to somewhat diluted bromine containing a little $N/2$-sodium hydroxide, rubbed with a glass rod, and diluted to 200—300 c.c. Sodium acetate (5 grams) and potassium iodide (0·5—1 gram), followed by a few c.c. of $N/4$-sulphuric acid to precipitate the iodine, are then added, after which it is titrated with thiosulphate solution in presence of starch solution. One c.c. of $N/10$-thiosulphate = 0·000761 gram of phosphoric anhydride. The bromine solution (Artmann, A., 1913, ii, 430) is prepared by adding 1400 c.c. of bromine water to a cooled $N/4$-sodium hydroxide solution (500 c.c.).

The titration can be done by artificial light. N. H. J. M.

Conventional Methods for Estimating Phosphoric Acid in Manures. F. Pilz (*Bied. Zentr.*, 1914, **43**, 601—608; from *Zeits. landw. Versuchswes. Oesterr.*, 1914, **17**, 55).—The direct citrate method, as employed in Austria for superphosphates, basic slag, and bone meal, gives satisfactory results without difficulty, whilst the German modification frequently gives conflicting results, owing partly to the employment of less concentrated solutions and of smaller amounts.

In the case of crude phosphates, mixed manures, and soils, etc., von Lorenz's method as modified at Bonn seems to be suitable.

N. H. J. M.

Recovery of Molybdic Acid. W. D. Brown (*J. Ind. Eng. Chem.*, 1915, **7**, 213—214).—Molybdic acid may be recovered from the filtrates obtained in estimations of phosphoric acid by heating the solution to boiling, adding an excess of sodium phosphate, and separating the yellow precipitate. A quantity of 210 grams of the latter is then dissolved in a mixture of 800 c.c. of water and 600 c.c. of ammonia, the solution is cooled, 35 grams of magnesium nitrate dissolved in 100 c.c. of water are added, the precipitated ammonium magnesium phosphate is separated by filtration, and the filtrate is mixed with 1900 c.c. of nitric acid (1 : 1); the yield is 3500 c.c. of molybdic acid reagent. W. P. S.

Iodometric Estimation of Arsenic after Precipitation as Metal. Lancelot Andrews (*Chem. Zeit.*, 1914, **38**, 983—984. Compare A., 1914, ii, 68).—A reply to Brandt (A., 1914, ii, 291). The author maintains the arguments previously advanced (*loc. cit.*) in favour of using stannous chloride instead of hypophosphorous acid to precipitate the arsenic. The precipitation occurs at a lower temperature; hence there is less risk of the arsenic volatilising as chloride, and, moreover, the possibility of phosphorus being precipitated from the hypophosphorous acid is obviated. G. F. M.

Iodometric Estimation of Arsenic after Precipitation as Metal. L. Brandt (*Chem. Zeit.*, 1914, **38**, 984).—A reply to Andrews (preceding abstract). The objections to the hypophos-

phorous acid method are not justified. Although arsenic in the arsenious state may be reduced by stannous chloride at a lower temperature than by hypophosphorous acid, yet when in the more frequently occurring arsenic state, it is not, and, moreover, the higher temperature is in no way detrimental. It is not denied that there is any possibility of the precipitation of phosphorus or that hypophosphorous acid cannot be obtained arsenic-free. G. F. M.

Estimation of Arsenic in Lead by Hypophosphorous Acid. L. BRANDT (*Zeitsch. öffentl. Chem.*, 1915, **31**, 66—71. Compare A., 1914, ii, 383).—The metal is dissolved in hydrochloric acid containing bromine, the excess is expelled by heating the solution, and, after cooling, 20 c.c. of hypophosphorous acid (D 1·15) and 50 c.c. of concentrated hydrochloric acid are added. The mixture is heated nearly to boiling for ten minutes, then boiled, the precipitated arsenic collected on a filter, washed with hot dilute hydrochloric acid, then with water, and its quantity estimated by titration with iodine solution. In samples containing a small quantity of arsenic a relatively large weight of the sample may be taken for the estimation, and the greater part of the lead separated as sulphate before the arsenic is precipitated by the addition of hypophosphorous acid. W. P. S.

Estimation of Carbon and Phosphorus in Cerium and Cerium Alloys. HANS ARNOLD (*Zeitsch. anal. Chem.*, 1914, **53**, 678—682).—For the estimation of total carbon the method of oxidation with a mixture of chromic acid and sulphuric acid is employed. When cerium, however, is brought into contact with this mixture, explosion is liable to occur unless the following procedure is adopted. Five grams of the metal are placed in the evolution flask and 60 c.c. of a 20% copper sulphate solution are added; the metal disintegrates gradually, and is coated with copper. The small quantity of hydrocarbon gases liberated at this stage are burnt to carbon dioxide by passing them over platinised asbestos. After about one hour, 30 c.c. of chromic acid solution (720 grams of chromic acid in 700 c.c. of water) are added, followed by the gradual addition of a mixture of 100 c.c. of sulphuric acid and 235 c.c. of water. The whole mixture is then boiled for two to three hours, and the process carried out as in the estimation of carbon in iron or steel. Free carbon is estimated by dissolving 10 grams of the metal in 100 c.c. of 30% copper chloride solution, adding 100 c.c. of ferric chloride solution (125 grams of ferric chloride dissolved in 150 c.c. of water and 100 c.c. of hydrochloric acid), and collecting the insoluble residue containing the carbon on an asbestos filter; the filter and its contents are washed, and the carbon then estimated by oxidation with chromic acid and sulphuric acid. The phosphorus is estimated by dissolving 10 grams of the metal in nitric acid, neutralising the solution, and precipitating the rare earths as oxalates. The filtrate from the latter is evaporated, the excess of oxalic acid decomposed with nitric acid, and the phosphoric acid precipitated with molybdic acid reagent. Four

samples of cerium were found to contain: total carbon, 0·058—0·150%; free carbon, 0·037—0·074%; carbide, 0·021—0·076%; phosphorus, a trace to 0·059%. W. P. S.

Estimation of Free Carbon Dioxide in Drinking Water. L. W. WINKLER (*Zeitsch. anal. Chem.*, 1914, **53**, 746—755).—Titration of the carbon dioxide with sodium carbonate solution (compare Tillmanns and Heublein, A., 1912, ii, 1211), using phenolphthalein as indicator (1 c.c. of a 1% solution per 100 c.c. of the water), yields trustworthy results, provided that a correction, depending on the hardness of the water, is applied. A table showing these corrections is given. W. P. S.

Estimation of Carbon Dioxide in Minerals. LEON H. BORGSTRÖM (*Zeitsch. anal. Chem.*, 1914, **53**, 685—687).—In the estimation of carbon dioxide in minerals, such as scapolite, etc., the addition of a small quantity of hydrofluoric acid to the hydrochloric acid used for the decomposition accelerates the rate at which the mineral is dissolved, and the carbon dioxide is evolved completely in about fifteen minutes. The results obtained are higher and more concordant than when hydrochloric acid is used alone; the hydrofluoric acid attacks the flask to some extent, but the same flask may be used for a considerable number of estimations. W. P. S.

Estimation of Soil Carbonates. A Modification. W. H. MACINTIRE and L. G. WILLIS (*J. Ind. Eng. Chem.*, 1915, **7**, 227—228).—Although dilute phosphoric acid solution is capable of decomposing the carbonates usually present in soils, and the whole of the carbon dioxide present may be expelled by shaking the soil with this acid for thirty minutes under reduced pressure, soils containing dolomite sometimes yield low results. The authors therefore recommend the use of *N*/10-hydrochloric acid in place of the phosphoric acid. The liberated carbon dioxide is absorbed in a tower containing sodium hydroxide solution. At the end of the experiment, the contents of this tower are titrated with sulphuric acid until neutral to phenolphthalein, and the carbon dioxide is estimated by continuing the titration to the neutral point of methyl-orange. W. P. S.

Estimation of Potassium by the Perchlorate Method. RUSSELL GIBSON THIN and ALEXANDER CHARLES CUMMING (T., 1915, **107**, 361—366).—Experiments have been made with a view of elucidating the causes and extent of possible errors in the perchlorate method for the estimation of potassium. Davis (*J. Agric. Sci.*, 1912, **5**, 52) suggested washing the precipitate with 95% alcohol containing 0·2% of perchloric acid, but solubility determinations indicate that potassium perchlorate is distinctly soluble in alcohol (0·051 gram in 100 grams 93·5% alcohol at 25·2°), and that the water added with the perchloric acid more or less counterbalances the slight decrease in solubility caused by the addition of the acid.

Another source of error is the presence of traces of potassium perchlorate in the so-called "pure" perchloric acid of commerce, which should therefore be redistilled in a vacuum before use. The authors conclude that accurate results may be obtained if the following conditions are complied with: Ammonium salts must not be present in any quantity. Evaporation with the perchloric acid must be carried far enough to ensure complete conversion of chlorides into perchlorates. A freshly-prepared saturated alcoholic solution of potassium perchlorate must be used as the washing liquid instead of alcohol and perchloric acid. G. F. M.

Volumetric Estimation of Small Amounts of Potassium. HERMANN FISCHER (*Landw. Versuchs.-Stat.*, 1914, **85**, 139—145).—Whilst Mitscherlich's method has been found to give satisfactory results, it remains to be ascertained whether the method proposed by Zaleski (A., 1914, ii, 147) is suitable with varying concentrations and in presence of other salts. N. H. J. M.

Estimation of Zinc in Ores and Wastes. HANS RUBRICIUS (*Chem. Zeit.*, 1915, **39**, 198).—A rapid method particularly suitable for the estimation of small quantities of zinc. Five grams of finely powdered substance are dissolved in 15 c.c. of concentrated hydrochloric acid, a little nitric acid being eventually added to complete the solution. After concentrating to a very small volume, 30 c.c. of concentrated ammonia are added to the cooled liquid, and the precipitated iron, after two or three further treatments with ammonia to ensure complete solution of the manganese and zinc, is filtered off, and the filtrate and washings to which a little copper sulphate solution is added, if copper was not originally present, are treated at 100° with a few crystals of sodium sulphide. A granular sulphide precipitate is thus obtained, which can readily be collected. It is treated with hot dilute hydrochloric acid, and the zinc in the soluble portion is precipitated with sodium carbonate and weighed as oxide. If manganese is present it is previously removed either by extracting the sulphide precipitate with acetic acid or by precipitating as hydrated dioxide from the chloride solution with ammonium persulphate or bromine immediately before throwing down the zinc with sodium carbonate. G. F. M.

Precipitation of Zinc and Manganese by Ammonium Sulphide. F. SEELIGMANN (*Zeitsch. anal. Chem.*, 1914, **53**, 594—595).—The following procedure is recommended for obtaining manganese or zinc sulphide in a condition in which it may be filtered without difficulty. The neutral solution, containing about 0·5 gram of manganese or zinc per 200 c.c., is rendered strongly ammoniacal (10—20 c.c. of 25% ammonia per 10 c.c. of solution), heated at 60—80°, and treated with a slight excess of ammonium sulphide. The mixture is then boiled for a few minutes, the precipitate collected on a filter, washed with dilute ammonium sulphide, and ignited. The ignited residue is treated with 5 c.c. of concentrated sulphuric acid, and the excess of this is removed by heating. Zinc

sulphate may be heated to dull redness without undergoing decomposition, and manganese sulphate is somewhat more stable.

W. P. S.

Analysis of Litharge. P. Beck (*Zeitsch. anal. Chem.*, 1915, **54**, 137—147).—A complete analysis of litharge is seldom required when the material is to be used for technical purposes, but the estimation of certain impurities contained in most specimens of litharge is of importance. For the estimation of copper 100 grams of the litharge are dissolved in nitric acid, the lead is separated as sulphate, and the solution diluted to 1 litre. According to the amount of copper present, a quantity of from 10 to 100 c.c. of this solution is treated with an excess of ammonia, aluminium and ferric hydroxides are separated by filtration, the filtrate is acidified with dilute sulphuric acid, and the copper deposited electrolytically. If the colour of the deposited copper indicates the presence of other metals, the deposit is dissolved in nitric acid, ammonia and ammonium carbonate are added, any precipitate of bismuth hydroxide is separated, and the copper again deposited electrolytically. Litharge for use in pottery and glass manufacture should contain not more than 0·004% of copper or more than 0·006% of iron. To estimate these two metals in one portion of the sample 100 grams of the latter are dissolved in nitric acid, the lead is separated as sulphate, the lead sulphate washed with dilute nitric acid, and the washings added to the filtrate, which is evaporated and heated to expel the nitric acid. After dilution, lead sulphate is again separated, and the copper is precipitated as sulphide; the copper sulphide is dissolved in nitric acid, evaporated with sulphuric acid, any traces of lead sulphate are separated, the solution is treated with ammonia and ammonium carbonate, bismuth hydroxide is separated, and the copper then precipitated as sulphide from a sulphuric acid solution. The copper sulphide thus obtained is collected and weighed as oxide. The iron is estimated gravimetrically in the filtrate from the first copper sulphide precipitate.

Litharge intended for use in the manufacture of accumulators should be free from nitrites or nitrates (the diphenylamine and brucine-sulphuric acid tests are recommended), and should not contain more than traces of iron, copper, or other metals precipitated by hydrogen sulphide; the chlorine-content must not exceed 0·05%. The quantity of metallic lead in litharge may be estimated by mixing 100 grams of the sample with 700 c.c. of water, adding 70 c.c. of nitric acid (D 1·4) in small quantities at a time, collecting the insoluble metallic lead on a filter, then dissolving it in hot dilute nitric acid, and estimating it either electrolytically or gravimetrically. Insoluble substances (lead sulphate, silica, etc.) are estimated by treating 100 grams of the litharge with 700 c.c. of water and 80 c.c. of nitric acid, heating the mixture until all the lead oxide has dissolved, collecting the insoluble portion on a filter, washing it six times with hot water, and then igniting it in a porcelain crucible.

W. P. S.

Comparison of Methods for the Analysis of the Higher Lead Oxides. JAROSLAV MILBAUER and BOHUMIR PIVNIČKA (*Zeitsch. anal. Chem.*, 1914, **53**, 569—580).—Bunsen's method, which depends on the reaction: $PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2$, yields results which are at the most 0·1% too low. The modification of Lux's method described by Chwala and Colle (A., 1911, ii, 441) tends to give results which are slightly too high, whilst Finzi and Rapuzzi's method (A., 1913, ii, 624) gives results which are too high by about 1·4%. The authors have attempted to estimate lead dioxide by a process based on the reaction:

$$PbO_2 + 2NH_2{\cdot}OH + 2KOH = Pb(OK)_2 + 4H_2O + N_2.$$

The reaction proceeds in the cold, but owing to the retention of nitrogen in the reacting solution, the results obtained are somewhat too low. W. P. S.

Rapid Electrolytic Estimation of Copper. WALTER THEEL (*Chem. Zeit.*, 1915, **39**, 179).—A shortening of the time required for the complete electrolytic deposition of copper by using a hot solution and a high current density (Koch, A., 1913, ii, 794) may be attained more simply by electrolysing in concentrated solution with a current of only 1—2 amperes. One gram of the metal or alloy is dissolved in fairly concentrated sulphuric and nitric acids, and after boiling off nitrous fumes the solution is diluted to 25 c.c. This is electrolysed in the usual way with net electrodes, and using 1·3 ampere the operation is completed in one hour, or with 2 amperes in forty-five minutes. Only a very slight further acceleration is obtained by warming the solution, and, in fact, above a certain optimum, namely, 44° with 1·3 ampere, or 49° with 2 amperes, a retardation sets in, and above about 60° copper is not deposited at all. G. F. M.

Estimation of Copper in Steel. W. D. BROWN (J. *Ind. Eng. Chem.*, 1915, **7**, 213).—The copper is precipitated as thiocyanate and this is titrated with potassium iodate solution. Five grams of the steel are dissolved in a mixture of 40 c.c. of nitric acid (D 1·20) and 25 c.c. of sulphuric acid (1 : 1), and the solution is heated to expel all nitric acid. When cold, the solution is diluted with 50 c.c. of water, boiled, diluted to 400 c.c. with hot water, 50 c.c. of concentrated ammonium hydrogen sulphite solution are added, followed by 25 c.c. of 5% potassium thiocyanate solution, the mixture is boiled for five minutes, and the precipitate collected and washed with 1% sulphuric acid. Filter and precipitate are transferred to a beaker, 20 c.c. of hydrochloric acid (1 : 1) and a quantity of standardised potassium iodate solution (2 c.c. for every 0·1% of copper expected) are added, the mixture is diluted to 500 c.c., potassium iodide solution added, and the liberated iodine titrated with thiosulphate solution. The potassium iodate solution employed should contain 19·64 grams of the salt per litre; 1 c.c. of the solution is equivalent to 0·005 gram of copper. W. P. S.

Estimation of Mercury in Urine. A. KLOTZ (*Zeitsch. physiol. Chem.*, 1914, **92**, 286—291).—The urine is completely oxidised in one

operation by heating on the water-bath with potassium chlorate and hydrochloric acid in the presence of a trace of osmium dioxide. The mercury salt is extracted with alcohol as in Salkowski's method (A., 1914, i, 630), and the mercury precipitated from the final aqueous solution on a strip of copper foil. After drying and weighing, the foil is heated in hydrogen, and the loss of weight due to the vaporisation of the mercury determined. By performing the latter operation in an "arsenic" tube, a mirror of mercury is formed even when the mercury is present in so small a quantity as to be incapable of being quantitatively estimated. H. W. B.

Estimation of Manganese in Soils. Bela von Horváth (*Zeitsch. anal. Chem.*, 1914, **53**, 581—593).—The colorimetric method described by Marshall, depending on the oxidation of manganese salts to permanganate by ammonium persulphate in the presence of silver nitrate (compare Schowalter, A., 1914, ii, 492), is recommended for the estimation of manganese in soils. The hydrochloric acid extract of the soil is twice evaporated to dryness with nitric acid to expel chlorine and destroy organic substances, the residue is then heated with sulphuric acid to remove the nitric acid, and the process proceeded with as described. Gravimetric and volumetric methods were found to be untrustworthy for the purpose. W. P. S.

Modified Method for the Gravimetric Estimation of Iron. Ladislaus Vásárhely (*Zeitsch. anal. Chem.*, 1914, **53**, 688—690).—Since ferric oxide tends to be reduced partly to magnetite (Fe_3O_4) during ignition owing to the reducing action of the carbon of the filter paper, the author recommends that precipitates of hydrated ferric oxide obtained in the usual way should be ignited in a Rose's crucible in a current of oxygen. W. P. S.

Volumetric Estimation of Iron in Hydrochloric Acid Solution by the Dichromate Method, using Diphenylcarbohydrazide as Indicator. L. Brandt (*Zeitsch. anal. Chem.*, 1914, **53**, 729—745).—In the method described previously by the author (A., 1914, ii, 71) sulphuric acid alone may be used in place of the manganese solution containing sulphuric and phosphoric acids. Arsenic, if present, must be oxidised previous to the titration of the iron. The correction for the amount of dichromate consumed by the indicator is quite small; it cannot be determined by a control titration of the indicator itself, but if this titration is made and a second quantity of the indicator added and titrated, the amount of dichromate used in the second titration will approximate to that used by the indicator in the titration of the iron. W. P. S.

Estimation of the Degree of Oxidation of Iron Compounds in Solutions containing Humus. E. Mäkinen (*Bied. Zentr.*, 1915, **44**, 78—79; from *Intern. Mitt. Bodenk.*, 1914, **4**, 388).—Owing to the presence of organic matter in soils, it is not possible to estimate

ferrous iron by oxidation methods. Ferric iron can, however, be estimated by reducing the solution in hydrochloric acid with stannous chloride, the end-point being indicated by the disappearance of the yellow colour; or an excess of stannous chloride may be added and titrated back with iodine in presence of starch solution. Only the latter process can be employed with soils.

The presence of humus is without effect on the results.

N. H. J. M.

Volumetric Estimation of Cobalt in the Presence of Nickel. ALBERT METZL (*Zeitsch. anal. Chem.*, 1914, **53**, 537—541).—The cobalt and nickel solution, which should not measure more than 100 c.c., is treated with 15 c.c. of 10% hydrogen peroxide, 30 c.c. of 5% sodium hydrogen carbonate solution, and 30 c.c. of sodium hydroxide solution for each 0·1 gram of cobalt present. The mixture is shaken, heated for twenty minutes to destroy the excess of hydrogen peroxide, the precipitate then dissolved by the addition of potassium iodide and sulphuric acid, and the liberated iodine titrated with thiosulphate solution. One mol. of iodine is equivalent to 1 mol. of cobalt. An alternative method depends on the different behaviour of cobalt and nickel towards ammonia, ammonium chloride, and oxidising substances. The solution of the two metals is treated with 10 c.c. of 16·6% ammonium chloride solution, 10 c.c. of ammonia, and 20 c.c. of 10% hydrogen peroxide, the mixture is heated for ten minutes, 50 c.c. of 25% potassium hydroxide solution are then added, and the solution is boiled for about forty-five minutes until all the ammonia has been expelled, water being added from time to time to compensate for loss by evaporation. The quantities of reagents mentioned are required for each 0·1 gram of cobalt. After cooling, the solution is treated with potassium iodide, acidified, and the liberated iodine titrated. The cobalt precipitate dissolves slowly, and the mixture should be shaken for about fifteen minutes after the addition of the potassium iodide and acid. Results are recorded which show that the method is trustworthy.

W. P. S.

Rapid Analysis of Alloys for Tin, Antimony, and Arsenic. F. A. STIEF (*J. Ind. Eng. Chem.*, 1915, **7**, 211—212).—A quantity of 0·5 gram of the alloy is dissolved in 8 c.c. of concentrated sulphuric acid, the solution is cooled, 5 c.c. of water, a small quantity of pumice-stone, and 20 c.c. of hydrochloric acid are added, and the mixture is distilled for fifteen minutes, the temperature of the vapour being maintained at 107°. The distillate, containing the arsenic trichloride, is collected in a bent-glass tube, cooled with water, the open end of which dips into water contained in a second vessel. After the addition of 2 grams of sodium hydrogen carbonate, the distillate is titrated with standardised iodine solution. The contents of the distillation flask are then cooled, diluted with 130 c.c. of water, and the antimony is titrated with permanganate solution. If the amount of antimony found is less than 14%, a quantity of antimony chloride is added to the solution

sufficient to increase the antimony-content to this limit, and the mixture is boiled for thirty minutes with the addition of 6 c.c. of sulphuric acid, 60 c.c. of hydrochloric acid, and about 6 inches of pure iron wire (14 gauge); another piece of iron wire is now added, and the boiling continued for a further thirty minutes. The flask is then closed, the contents cooled rapidly to about 20°, diluted with boiled water to 350 c.c., and the tin titrated with permanganate solution. The presence of copper has no effect on the titration of the antimony, but when the quantity of copper exceeds 3%, 1 gram of potassium iodide should be added immediately before the tin is titrated.

Antimony and tin may be estimated in materials containing large amounts of copper, iron, and arsenic, by dissolving 0·5 gram of the sample in 10 c.c. of sulphuric acid, 15 c.c. of water being added first if much silicon is present. The solution is heated until fumes of sulphuric acid appear, cooled, treated with 10 c.c. of water and 10 c.c. of hydrochloric acid, are boiled for two minutes, 1·5 grams of potassium chlorate are then added in small quantities at a time, and the mixture is heated until all chlorine has been expelled. The mixture is then boiled for about thirty minutes with the addition of 0·1 gram of sulphur, cooled, 6 c.c. of water, 20 c.c. of hydrochloric acid, and a small quantity of pumice-stone are added, the arsenic is expelled by boiling, and the antimony and tin are then estimated as described. W. P. S.

Separation of Gold and Platinum from other Metals. A. CHRISTENSEN (*Zeitsch. anal. Chem.*, 1915, **54**, 158—159).—The method proposed depends on the fact that gold and platinum are reduced to the metallic state by hydrazine hydrochloride; whilst gold is reduced in the cold, platinum is reduced only when the mixture is heated. The solution containing the two metals is rendered slightly acid with hydrochloric acid, an excess of hydrazine hydrochloride is added, and the mixture is heated for one hour on a water-bath. The precipitated metals are separated, washed with hot nitric acid to remove mercury and copper, then dissolved in aqua regia, and the gold and platinum identified by the usual tests. The filtrate from the gold and platinum precipitate may be used for the detection of other metals; if Petersen's method (A., 1910, ii, 654) is used for this purpose, the excess of hydrazine hydrochloride must be removed previously by evaporating the solution and igniting the residue. W. P. S.

Estimation of the Reducing Power of Natural Waters. L. W. WINKLER (*Zeitsch. anal. Chem.*, 1914, **53**, 561—564).—The quantity of permanganate reduced in alkaline solution by natural water (compare A., 1902, ii, 701) is estimated by treating 100 c.c. of the water, diluted if necessary, with 10 c.c. of alkaline $N/100$-permanganate solution; after twenty-four hours the mixture is acidified with sulphuric acid, potassium iodide is added, and the liberated iodine titrated with thiosulphate solution. The following procedure is recommended for waters containing nitrites, ferrous salts,

and manganese salts: One hundred c.c. of the water are treated with 1 c.c. of 10% sodium hydroxide solution, and set aside for five minutes; ferrous and manganous salts are thus oxidised by the dissolved oxygen in the water. The potassium permanganate solution is added, and after the lapse of twenty-four hours the mixture is acidified with 25% phosphoric acid solution (this is preferable to sulphuric acid as it prevents the action of the ferric salts on potassium iodide), potassium iodide is added, and the iodine titrated with thiosulphate. Another portion of the water is also treated with sodium hydroxide solution to oxidise the ferrous and manganous salts, permanganate solution is then added, and the excess titrated after two minutes' contact. The nitrites are thus oxidised, whilst the organic matter is not appreciably attacked; the result is a measure of the substances, other than organic matters, which reduce permanganate. W. P. S.

Separation of Gases by Fractional Distillation in a Vacuum at Low Temperatures. G. A. Burrell and I. W. Robertson (*J. Ind. Eng. Chem.*, 1915, **7**, 209—210. Compare A., 1914, ii, 741; this vol., ii, 109).—A summary of the results so far obtained by the use of this method. A mixture of methane, ethane, propane, and butanes may be separated by liquefying the mixture with liquid air and removing the methane at this temperature; ethane is removed at −140°, propane at −120°, and butanes at −95°, leaving pentanes or higher paraffins as a residue. In a mixture of olefines, ethylene is removed at −140°, propylene at −120°, butylenes remaining as a residue. Benzene may be separated from air or coal gas at −78°. Water vapour in air may be estimated at a temperature of −78°, at which point the vapour pressure of ice is practically zero. The method will probably be of use in the examination of the various mixtures produced in the destructive distillation of fuels, etc. W. P. S.

Rapid Method of Fractionating Gases at Low Temperatures. G. A. Burrell and I. W. Robertson (*J. Ind. Eng. Chem.*, 1915, **7**, 210—211).—The gas, for example, coal gas, is liquefied with liquid air, and as much gas as possible is removed at this temperature and collected; other fractions are obtained from the residue at −140°, −120°, and −78° respectively. The first distillate is then refractionated at the temperature of liquid air, the second distillate is added to the residue and fractionated at −140°, and so on. The last residue obtained at −78° is allowed to evaporate at the ordinary temperature and its pressure ascertained. At −78° practically the only gas remaining in coal gas is benzene. W. P. S.

Analytical Distillation of Petroleum. W. F. Rittman and E. W. Dean (*J. Ind. Eng. Chem.*, 1915, **7**, 185—195).—An account is given of the first section of a series of experiments dealing with the analytical distillation of petroleum, the investigation having been commenced for the purpose of securing data which will aid

in the formulation of a standard method. The methods at present studied are those of Allen and Jacobs, Ubbelohde, and Hempel, and it is found that the most efficient of these, the Hempel method, gives but a low degree of separation. An increased efficiency might be obtained by using a longer Hempel column, but this would make it so effective as a reflux apparatus that the higher boiling fractions could not be distilled without the occurrence of a considerable amount of "cracking." Distillation through a Hempel column of moderate height gives a degree of fractionation more than twice that attained by the use of an ordinary open flask, whilst the Allen and Jacob method (minimum condensation) is as far below the open-flask method in efficiency as the latter is below the Hempel method. The degree of separation obtained by any one method of distillation is not a constant factor, but increases as the temperature rises. Similarities between the results obtained by various methods of distillation are entirely superficial, as is shown by the results of a series of refractionation experiments.

W. P. S.

Detection and Estimation of Petroleum Derivatives in Turpentine Oils. C. GRIMALDI and L. PRUSSIA (*Chem. Zeit.*, 1914, **38**, 1001—1002).—Of chemical methods for the detection of petroleum or coal-tar derivatives in turpentine oils oxidation of the terpenes by means of mercuric acetate is to be preferred. In a 500 c.c. flask with a graduated neck are placed 75 grams of mercuric acetate, 200 c.c. of water, 100 c.c. of glacial acetic acid, and 10 c.c. of the turpentine. After heating under reflux for two hours at 80°, dilute nitric acid (2 vols. acid D 1·4, 1 vol. water) is added to the cooled mixture up to the zero mark. In the absence of petroleum derivatives the solution will be homogeneous, but otherwise unoxidised oil will be present, and its volume may be read off after it has collected completely in the neck. The minimum quantity of petrol that can be detected varies from 6—12%, of turpentine substitutes from mineral oils 8—10%, and of paraffin 10%. With coal-tar derivatives, satisfactory results have not yet been obtained.

G. F. M.

A Solution of Vanillin in Hydrochloric Acid as Reagent for Essential Oils. J. J. CERDEIRAS (*Anal. Fis. Quim.*, 1915, **13**, 46—54).—A series of tables giving the colour reactions produced by the interaction of vanillin in hydrochloric acid and a number of essential oils.

A. J. W.

Estimation of Lipoids in Serum. W. KLEIN and L. DINKIN (*Zeitsch. physiol. Chem.*, 1914, **92**, 302—330).—See this vol., i, 340.

The Separation of Sterols from Fats by means of Digitonin. P. BERG and J. ANGERHAUSEN (*Chem. Zeit.*, 1914, **38**, 978—979. Compare A., 1913, ii, 885; 1914, ii, 503).—The following method of procedure is recommended in the digitonin process for separating phytosterol, etc., from fats: 50 grams of fat are shaken

in a separating funnel at 70° with 20 c.c. of 1% alcoholic digitonin solution for fifteen minutes; 20 c.c. of chloroform are then added, and after shaking and allowing to separate, the lower layer is run off. The upper alcoholic layer containing the precipitated digitonide is filtered, the residue washed three or four times with ether, and transferred with 50 c.c. into a conical flask. After well shaking, it is again collected, washed again several times with ether on the filter, and the fat-free residue is acetylated by boiling for fifteen minutes with 3 c.c. of acetic anhydride. On cooling, crystals of the steryl acetate are deposited; they are collected, washed with 70% alcohol, and dissolved off the filter with ether. The residue obtained by evaporating the ether is finally crystallised from absolute alcohol.

The advantages claimed are the more perfect removal of adhering fat from the digitonin compound, so that the steryl acetates, after but one crystallisation, are quite free from fat, and hence never exhibit abnormally low melting points, and secondly, greater facility in filtering the precipitate, since unchanged digitonin is not precipitated, being held in solution by the chloroform.

The substance left after the removal of the sterols from the unsaponifiable portion of the fats has also been investigated. The unsaponifiable portion, separated by Bömer's method, was treated with excess of digitonin solution, and the filtrate evaporated to dryness and extracted with ether to dissolve out sterol-free substance from the unaltered digitonin. From lard, 0·032% of a soft, yellow mass was obtained, which was optically inactive. Mowrah fat gave 1·48% of a resinous substance, which had a specific rotation of +34°. The optical inactivity of this residue from animal fats, and the converse with vegetable fats, is apparently general, at least so far as the present investigations have extended. G. F. M.

Direct and Invert Polarisation of Pure Sucrose. Herbert S. Walker (*J. Ind. Eng. Chem.*, 1915, **7**, 216—217).—From the results of experiments with pure sucrose it would appear that the Clerget factor, if designed to give a reading of 100% for sucrose with the present sugar scale, should be increased from 142·66 to 142·78, whilst if it is intended to give the same figure as the direct polarisation of sucrose, regardless of the scale used, it should be further increased to 142·92. W. P. S.

Estimation of Sucrose in Beetroots which have been Frozen and Thawed. Émile Saillard (*Compt. rend.*, 1915, **160**, 360—363).—Beetroots which have been frozen and subsequently thawed yield a juice which is much more acid than the ordinary beetroot, and has a lower viscosity. Such roots have lost a considerable portion of their original sugar by fermentation, and those roots which contain a higher proportion of reducing sugars have a low sucrose-content. These roots contain one or more substances hydrolysable by hydrochloric acid, but not acted on by sucrose, and consequently this biochemical agent must be used for inversion to arrive

at the true sucrose-content. The alcohol furnished by the fermentation of these frozen and thawed beetroots arises in part from the hydrolysable substances, other than sucrose, which can be slowly transformed into reducing sugars, capable of being fermented, under the influence of the acids in the fermented juice at 28—30°.
W. G.

Estimation of the Total Fatty Acids and other Ether-soluble Constituents of Feedstuffs. J. B. RATHER (*J. Ind. Eng. Chem.*, 1915, **7**, 218—220).—The unsaponifiable substances are estimated as described previously (this vol., ii, 113). The alkaline aqueous soap solution resulting from this estimation is then heated to expel dissolved ether, cooled, acidified with 8 c.c. of glacial acetic acid, and extracted four successive times with light petroleum. The solution of the fatty acids in light petroleum is then washed twice with water, the washings are extracted with light petroleum, the extract is added to the main bulk, which is then evaporated, and the residue of fatty acids dried to constant weight. The aqueous solution from the fatty acids is acidified with hydrochloric acid, extracted with ether, the ethereal solution evaporated, and the residue weighed. This residue contains the unsaponifiable substances which are soluble with difficulty in light petroleum; chlorophyll, when present, is found in this fraction. When applied to fodders and excrements, the method yields higher results than are obtained by extraction with ether; in the case of hays and excrements the results are about twice as high. W. P. S.

Estimation of Tartaric Acid in Beverages, especially in Wines. E. P. HÄUSSLER (*Zeitsch. anal. Chem.*, 1914, **53**, 542—560).—Examination of various methods showed that Halenke and Moslinger's method yields trustworthy results, but in the case of beverages containing but little, if any, tartaric acid, the correction of 0·225 gram of tartaric acid is misleading. Villiers and Collin's modification of Berthelot and Fleurieu's method (precipitation of the tartaric acid by the addition of potassium bromide and alcohol, and titration of the resulting potassium hydrogen tartrate) is also trustworthy even in the case of slightly plastered wines. The racemate method (A., 1911, ii, 666) was only applied in a few cases, and its accuracy was not definitely ascertained; this method appears to be tedious and costly. W. P. S.

Degradation of Cholesterol in Animal Organs. VII. Bile Acids. I. LIFSCHÜTZ (*Zeitsch. physiol. Chem.*, 1914, **92**, 383—401. Compare A., 1914, i, 1019).—The author describes a new method for estimating the cholic acids in bile. 0·5 Gram of the concentrated bile is dissolved in 10 c.c. of hot glacial acetic acid and oxidised with 0·5 gram of benzoyl peroxide. After bringing to 20 c.c. with glacial acetic acid, 1 c.c. is diluted with 5 c.c. of chloroform, and 1 c.c. of the diluted liquid treated with 2 c.c. of acetic acid–sulphuric acid (10 vols. glacial acetic acid to 1 vol. sulphuric acid) and 1 drop of a 2·5% solution of ferric chloride in glacial

acetic acid. The deep green liquid thus obtained has a pronounced absorption band in the red, and 1 c.c. is now diluted with glacial acetic acid until this absorption band is only just visible. A weighed quantity of pure crystallised cholic acid is now treated in a similar way, and the dilution at which the absorption band is only just visible again determined. The ratio of the two dilutions, calculated to the quantities of material originally weighed out in each case, multiplied by 100, gives the percentage of cholic acid in the bile.

The results obtained by this new method have been checked by a gravimetric method, and agree remarkably well.

The author confirms the view previously put forward (*loc. cit.*) that cholic acid and cholesterol on oxidation with benzoyl peroxide and treatment with the acetic acid–sulphuric acid and ferric chloride reagents give products with identical absorption spectra. The cholic acid in bile salts arises, therefore, from cholesterol.

H. W. B.

The Precipitation of Amino-acids by Mercuric Acetate and Sodium Carbonate. C. Neuberg and Joh. Kerb (*Biochem. Zeitsch.*, 1914, **67**, 119—121).—The mercuric acetate–sodium carbonate reagent employed by the authors for the precipitation of amino-acids also precipitates polypeptides and peptones. This statement is illustrated by experiments on the precipitation of leucyl-leucine, glycyltryptophan, glycyltyrosine, and the peptone of silk-fibroin and Witte's peptone.

S. B. S.

The Triketohydrinden Reaction. C. Neuberg (*Biochem. Zeitsch.*, 1914, **67**, 56—58).—The author has already called attention to the fact that many substances other than the amino-acids yield this reaction. He now adds the following to the list: Thiosulphuric acid; sulphoxyarsenic acid, H_3AsO_3S; selenious acid; hydrogen sulphide; the metals magnesium, zinc, and aluminium, and the following organic substances: ammonium formate, ammonium thiolactate, ammonium thioglycollate, and chloral hydrate after addition of ammonia and evaporation of the excess. The conditions for producing the reaction are described, and attention is called to the fact that most of the substances have a reducing action.

S. B. S.

Analysis of Ethyl Acetate. P. Szeberényi (*Zeitsch. anal. Chem.*, 1914, **53**, 683).—The ester-content is found by saponification. A quantity of 25 grams of the acetate is then saponified with aqueous alkali solution, distilled, and the alcohol estimated in the distillate; the quantity of alcohol thus found represents that present both in the combined and free state in the sample, and the amount of free alcohol is calculated. The quantity of water present in the sample is found by difference. The total amount of alcohol may also be found by oxidising the sample directly with potassium dichromate solution in the presence of sulphuric acid. One c.c. of $N/2$-potassium dichromate solution corresponds with 5·7625 mg. of

ethyl alcohol. In this estimation the combined alcohol is oxidised as well as the free alcohol, if the latter is present, whilst the acetic acid liberated is not attacked. W. P. S.

Approximate Estimation of Non-volatile Unsaponifiable Substances in Linseed Oil Varnish. F. BÁRÁNY (*Zeitsch. anal. Chem.*, 1914, **53**, 684—685).—The presence of appreciable quantities of mineral oil or resin oil in the varnish may be detected, and the amount estimated by boiling 10 grams of the sample for twenty minutes with 30 c.c. of alcohol and 5 c.c. of aqueous 50% potassium hydroxide solution. The solution is then transferred to a graduated cylinder, diluted with alcohol to 50 c.c., and shaken with 100 c.c. of light petroleum. After the addition of 100 c.c. of water, the mixture is again shaken gently, and 50 c.c. of the light petroleum layer are withdrawn, evaporated, the residue dried at 100°, and weighed. W. P. S.

Titration of Milk with Alcohol of Different Strengths. F. LÖHNIS (*Bied. Zentr.*, 1914, **43**, 640—642; from *Molk. Zeit.*, 1914, **28**, 153).—Whilst fresh milk from single cows gives very variable results when titrated with alcohol, the results with mixed milk are more satisfactory. When the amount of 80% alcohol exceeds 4 c.c. (to 2 c.c. of milk), a low amount of germs is indicated. With a medium amount of germs, the amount of alcohol will be 2—4 c.c., whilst less than 2 c.c. will be required when the number of germs is high. In more extreme cases less than 2 c.c. of 70% alcohol will be required. The method, with such modifications as may be found desirable, should be useful as a quick method of ascertaining the amount of germs present and the keeping quality of milk.
N. H. J. M.

Alcohol Reaction of Milk. AUGUST AUZINGER (*Bied. Zentr.*, 1914, **43**, 645—646; from *Molk. Zeit.*, 1914, **28**, 457. Compare Löhnis, preceding abstract).—Normal milk to which a small amount of fresh rennet has been added, at once gives with 68% alcohol a precipitate, indicating that rennet causes an immediate change in milk, liberating calcium salts. The greater the amount of soluble calcium salt present the sooner is coagulation produced by alcohol. Most single samples of milk fail to coagulate with alcohol after being boiled, if the acidity is normal. Addition of various substances, such as sodium fluoride, ammonium oxalate, formaldehyde, etc., interferes with the alcohol test; substances which precipitate calcium prevent coagulation, whilst addition of soluble calcium salts increases coagulation. The milk of cows fed with calcium phosphate, coagulated with alcohol of lower percentage than milk from control cows.
Alcohol of 70% (by vol.) is recommended. N. H. J. M.

Methods of Estimation of Lecithin in Milk. N. A. BRODRICK-PITTARD (*Biochem. Zeitsch.*, 1914, **67**, 382—390).—According to Burow (A., 1901, ii, 30), the lecithin in milk can be estimated by

dropping it into a mixture of equal parts of alcohol and ether acidified with acetic acid. The filtrate is evaporated at a low temperature, and extracted with dry ether. The phosphorus is then estimated in the ethereal extract. According to the author, this process is liable to lead to inaccurate results if the residue which is extracted is not first dried, and this can be accomplished by the addition of anhydrous sodium sulphate. The content of lecithin is found to vary with the period of lactation and the individual, and increases with the increasing fat-content of the milk.

S. B. S.

Estimation of Citral in Concentrated Oil of Lemon. E. Böcker (*J. pr. Chem.*, 1914, [ii], **90**, 393—404).—Concentrated oil of lemon is adulterated principally by addition of citral derived from lemon-grass oil. Such addition does not increase the content of volatile, oxygenated compounds, on which the value of the oil as a perfume depends. The citral-content of these oils may be determined with a considerable degree of accuracy by the sodium sulphite method devised by Burgess (A., 1904, ii, 371), methods in which sodium hydrogen sulphite is used giving erroneous results. The proportion of citral present is not sufficient to indicate addition of citral, but, taken in conjunction with the hydrocarbon-content of the oil (compare A., 1914, ii, 301), it will show if the proportion added is large. The highest percentage of citral found in oil of lemon free from terpenes and sesquiterpenes is 66, the content varying inversely with the hydrocarbons present. Consequently, if an oil of lemon contains either no hydrocarbons and more than 66% of citral or 50% of hydrocarbons and more than 33% of citral, addition of the latter must have occurred. Since, however, the genuine hydrocarbon-free oil usually contains less than 66% of citral, the above method gives no more than the minimal value of the adulteration, and may, unless the latter amounts to about 20%, not detect it at all.

T. H. P.

Reactions of Vanillin. E. P. Häussler (*Zeitsch. anal. Chem.*, 1914, **53**, 691—695. Compare A., 1914, ii, 592).—When albumin, casein, peptone, or fibrin is treated with a small quantity of dilute alcohol and evaporated with the addition of vanillin, as in a test described previously (*loc. cit.*), a yellow coloration is obtained which changes to violet when treated with hydrochloric acid and again evaporated. Blue or violet colorations are obtained by subsequent treatment with ammonia and then with hydrochloric acid. Urea yields a yellow coloration when evaporated with vanillin and the residue treated with hydrochloric acid, and a red coloration after treatment with ammonia and hydrochloric acid. The colorations obtained under similar conditions with gelatin are brown.

W. P. S.

Experiments on the Resistance of Morphine towards Putrefaction. F. Doepmann (*Chem. Zeit.*, 1915, **39**, 69—71).—Four 1 kilo. portions of horseflesh were intimately mixed with 200, 100, 50, and 20 mg., respectively, of morphine hydrochloride, and frac-

tions of each were examined quantitatively for morphine at intervals of one, two and a-half, five and a-half, and eleven months. Although it was found that the presence of putrefactive bases prevented a trustworthy estimation of the amount of morphine, yet the alkaloidal residue was obtained in a sufficiently pure state for the direct application of the qualitative colour reactions, all of which gave a distinct positive result, showing that even after eleven months' putrefaction, unchanged morphine was still present. In the series examined at the end of a month, the morphine was actually obtained in a solid, crystalline condition by precipitation from the chloroform solution with light petroleum. Physiological tests were also made on mice with the residues obtained from portions containing 40 and 10 mg., respectively, after eleven months' putrefaction. Positive results were observed with the first residue, but in the second only traces of morphine sufficient to give the colour reactions could have been present, as the physiological test did not respond. For the extraction of the morphine, Husemann's method with some modifications was adopted, as follows. The flesh was treated with a litre of water acidified with acetic acid, first in the cold and then for some hours on the water-bath, whereby albumin was coagulated. After filtering through linen, the residue was once more treated in a similar way. The united filtrates, after concentration, were subjected to precipitation, first with alcohol and then with lead acetate, avoiding an excess. From the filtrate and washings the excess of lead was removed by hydrogen sulphide, and the clear solution, after concentration to 100 c.c., extracted with warm chloroform, after addition of ammonia in slight excess. The chloroform residues were dissolved in a small quantity of dilute sulphuric acid, and extracted once with pure amyl alcohol, which removed coloured impurities. The morphine was then transferred to chloroform solution, back to water, and finally to chloroform again, and in this way a colourless to pale yellow residue was obtained, free from any impurities which would interfere with the colour reactions.

G. F. M.

Chemical Detection of Blood. Domenico Ganassini (*Boll. Chim. Farm.*, 1914, **53**, 777—781. Compare A., 1911, ii, 556).—The author has investigated Baecchi's test for blood (*Arch. Int. Méd. Légale*, 1913, **4**, 163), which is carried out as follows. Two c.c. of an aqueous alizarin-*S*-blue solution diluted to a mahogany-yellow colour are mixed with about one-half the volume of 3% hydrogen peroxide solution. A little of the liquid to be tested is then poured slowly down the wall of the test-tube. If blood is present, gentle shaking rapidly renders the liquid intensely blue, the blue colour slowly fading and giving place to a red colour, which is moderately stable. This reaction is stated to give a positive result with 1 part of blood in 20,000, and to answer well with blood which has undergone alteration and become insoluble in water, the blood being then first dissolved in alcohol acidified with hydrochloric acid.

The author finds that this test is very rapid and simple, but not specific, since it is given by soluble iron salts, especially ferrous sulphate and hydrogen carbonate even in minimal traces, and also by potassium iodide, chrome alum, free chromic acid, and ferratin. Nitrous or iodic acid gives the blue coloration in absence of hydrogen peroxide, which changes the colour to red and then to yellow. Many animal and vegetable organic compounds fail to respond to Baecchi's test, which in any case is completely successful only in faintly acid liquids, carbonic acid being sufficiently strong for this purpose.

This test can be regarded as of value only when it yields negative results. T. H. P.

A New Method for Determining the Activity of Diastase. Ottomar Wolff (*Chem. Zeit.*, 1915, **39**, 105—107).—The method is an optical one depending on a determination of the difference in the refraction of the initial starch and resulting sugar solutions by means of the Zeiss interferometer, already described by Habor and Löwe (*Zeitsch. angew. Chem.*, 1910, **23**, 1393). This apparatus has hitherto only been used with solutions of crystalloids, but it is now found that the concentration of colloidal solutions can be determined with the same exactitude, and, further, that the shifting of the interference bands is strictly proportional to the amount of sugar solution present in mixtures containing varying proportions of 1% sugar and starch solutions when compared with a standard 1% starch solution in the other chamber of the interferometer. For the measurement of diastatic activity, the procedure is as follows: 0·2 gram of diastase is added to each of two 50 c.c. portions of a 1% starch solution. One portion is boiled to destroy the ferment, and the other placed in a water-bath at 38° for two hours or longer. Both solutions are then filtered through dry filter papers, and compared in the interferometer, the shifting of the bands, measured by a micrometer screw gauge, being proportional to the amount of starch converted. An example is also given of a determination of the diastatic action of saliva.

G. F. M.

Methods of Soil Investigation. O. Albert and R. Bogs (*Bied. Zentr.*, 1915, **44**, 3; from *Internat. Mitt. Bodenk.*, 1914, **4**, 181).—The results of estimations of water in soils by Schwalbe's method (distillation with xylene) agreed with those obtained by the slower method of Mitscherlich (drying in a vacuum over phosphoric oxide). Both methods, preferably Schwalbe's, are suitable for loams, clay and peaty soils, whilst sandy soils need only be dried in an air-bath at 105—106°.

For estimating the sp. gr. of soils, the method is recommended in which the soil (20 grams), in a 50 c.c. flask, is treated with turpentine until all the air is expelled, after which the flask is filled with turpentine to the mark. The turpentine is run in from a burette, and the amount required to fill the flask ascertained. N. H. J. M.

General and Physical Chemistry.

Spectrochemical Investigations. K. von Auwers (*Annalen*, 1915, **408**, 212—284).—The D_4^{20} and n^{20} values for the α-, D-, β-, and γ-lines are given for a large number of derivatives (aldehydes, ketones, esters, hydroxy-compounds and their ethers) of benzene, *cyclo*pentadiene, furan, thiophen, coumarone, thionaphthen, and coumaran, and the exaltations of the specific refraction and dispersion have been calculated. The results present such obvious regularities that the tenability, within definite limits, of the following generalisations may be regarded as proved. (1) The spectrochemical character of the parent substance is only slightly, or not at all, changed when a methyl group enters the molecule of an aromatic aldehyde, ketone, or monocarboxylic ester in the ortho- or meta-position; its introduction in the para-position, however, markedly increases the exaltation. (2) Similarly, a methoxy-group in the ortho- or meta-position may considerably increase the exaltation, but its effect in the para-position is extraordinarily more powerful. (3) In consequence of these differences, para-derivatives of the types mentioned are readily distinguished from ortho- and meta-isomerides, but the differentiation of the latter by the spectrochemical method is frequently impossible. (4) The ethers of aromatic hydroxy-aldehydes, -ketones, and -esters exhibit considerably smaller exaltations than the parent substances. (5) *cyclo*Pentadiene, furan, and thiophen are spectrochemically similar, but not completely equivalent, structures. The optical depression exhibited by the three substances, which must be attributed to the presence of the 5-ring containing a conjugated system of double linkings, is diminished or is changed to an exaltation by the introduction of substituents; the effect of the same substituent is different in the two structures (data are lacking in the case of *cyclo*pentadiene). (6) Derivatives of coumarone and of thionaphthen exhibit almost the same specific exaltations. A methyl or methoxy-group in position 2 does not exert any influence, although it is present as a disturbing substituent in a conjugated system. The spectrochemical behaviour of ethyl coumarilate is not materially changed by the introduction of a methyl or methoxy-group in position 2. On the contrary, the exaltations of the coumarans are diminished by the introduction of a methyl group in position 4, that is, in the conjugated system.

The following new compounds are described. m-*Tolylmethylcarbinol*, $C_7H_7\cdot CHMe\cdot OH$, prepared from the aldehyde and magnesium methyl iodide, has b. p. 108·9—109·4°/12 mm., D_4^{20} 0·993, n_α 1·52262, n_D 1·52635, n_β 1·53740, n_γ 1·54710 at 15·35°, n_D^{20} 1·5243; p-*anisyl* iso*propyl ketone*, $OMe\cdot C_6H_4\cdot COPr^\beta$, has b. p. 149—150°/14 mm., D_4^{20} 1·047, n_α 1·53328, n_D 1·53925, n_β 1·55489, n_γ 1·56926 at 16·6°, n_D^{20} 1·5377; 4-*hydroxy*-m-*tolyl* iso*propyl ketone* has b p. 125·0—125·3°/11 mm., D_4^{20} 1·043,

n_D^{20} 1·5360, and its *methyl ether* has b. p. 155°/25 mm., D_4^{20} 1·016, n_D^{20} 1·5183; 4-*methylthionaphthen*, $C_6H_3Me<\overset{CH}{\underset{S}{}}>CH$, prepared by reducing the 2-hydroxy-compound with zinc and acetic acid, has b. p. 111—115°/12 mm., m. p. 19—22°, D_4^{20} 1·113, n_D^{20} 1·6155.

C. S.

Dispersion of Air and Oxygen in the Infra-red. C. Stătescu (*Bull. Acad. Sci. Roumanie*, 1914–15, **3**, 211—216).—The refractive index of dry atmospheric air and oxygen has been determined for wave-lengths between 5894·6 (Na) and 40,000 Ångström units. The method of Paschen is adopted in the measurements, a full account of which is to be published shortly (*Phil. Mag.*). The measurements were made with a gas pressure of about 1430 mm. Hg. It is shown that there is no anomalous dispersion observable in the case of air up to wave-lengths of 4·7 μ, but that at this value the presence of the carbon dioxide makes itself noticeable. In the case of oxygen, the dispersion is also normal. Tables of comparative values for both air and oxygen are given up to $\lambda = 86784$ Å.U., which are taken mainly from the work of Koch (A., 1905, ii, 661).

J. F. S.

Effect of Pressure on Arc Spectra. V. Nickel λ 3450 to λ 5500, including an Account of the Rate of Displacement with Wave-length, of the Relation between the Pressure and the Displacement, of the Influence of the Density of the Material and of the Intensity of the Spectrum Lines on the Displacement, and of the Resolution of the Nickel Spectrum into Groups of Lines. W. Geoffrey Duffield (*Phil. Trans.*, 1915, [*A*], **215**, 205—252. Compare A., 1911, ii, 350).—By the method described in a previous paper, the influence of pressure on the arc spectrum of nickel has been investigated by the application of pressures ranging from 10 to 100 atmospheres for the region λ 3450 to λ 4050 and λ 4600 to 5120, from 10 to 200 atmospheres between λ 4050 and λ 4600, and 10 to 75 atmospheres between λ 5120 and λ 5500. The observations are discussed in detail, with special reference to the displacement, broadening, reversal, and change in the relative intensities of the lines.

The relation between the displacement and the pressure is an approximately linear one, although the displacement per atmosphere is almost invariably greater at low pressures. According to the magnitude of the displacement, the nickel lines can be divided into two groups, which are also more or less sharply distinguished in regard to other pressure effects. The further characters of the lines suggest, however, a further division of the first group into two sub-groups. For the three groups thus obtained, the values of the displacement constants d/λ^2 or d/λ^3 are very approximately in the ratio 1 : 2 : 4. The separation into groups is more clearly shown by the ratio d/λ^2, but if the results for pressures greater than 10 atmospheres are alone considered, there is but little difference between the results obtained by the use of d/λ^2 or d/λ^3.

H. M. D.

Flame Reactions. IV. Wilder D. Bancroft and Harry B. Weiser (*J. Physical Chem.*, 1915, **19**, 310—330. Compare A., 1914, ii, 317, 398; this vol., ii, 2).—A description is given of a simple form of sprayer for introducing the spray of salt solutions into flames, and of apparatus for burning hydrogen in chlorine and chlorine in hydrogen. These have been used in the investigation of the flame spectra of salts of the alkali metals under different conditions.

In addition to the line spectrum, it has been found that salts of lithium, sodium, and potassium yield a continuous spectrum in the Bunsen flame. The continuous spectrum is of maximum intensity in the blue or blue-green region.

The blue luminescence of sodium, unaccompanied by yellow, is obtained when sodium salts are introduced into a hydrogen flame burning in chlorine; when metallic sodium burns slowly in oxygen, chlorine, or bromine; when a sodium salt is fused; when cathode rays act on sodium chloride; when anode rays first act on sodium chloride; when the coloured substance, obtained by the action of anode or cathode rays on sodium chloride, is heated; and when sodium chloride is precipitated rapidly from aqueous solution by the addition of hydrochloric acid or alcohol.

The yellow luminescence, accompanied by the fainter blue, is found to be emitted when a sodium salt is introduced into the Bunsen flame, when sodium burns rapidly in oxygen, chlorine, or bromine, and when canal rays act on sodium chloride.

From these observations, the conclusion is drawn that the blue luminescence is connected with the transformation of the sodium ion into undissociated sodium salt, and the yellow luminescence with the conversion of sodium atoms into ions.

The diminished intensity of the line spectra in the hydrogen chlorine flame, or in the Bunsen flame into which hydrogen chloride or ammonium chloride is introduced, is supposed to be due to a diminution in the extent to which the salts are chemically dissociated. Under these conditions, ionic dissociation takes place, but chemical dissociation is restricted. The behaviour of the line spectrum and of the continuous spectrum in an electrical field is consistent with the above views relating to the origin of these spectra. H. M. D.

Absorption Spectra of Various Halogen and Nitrile Derivatives of Benzene and Toluene as Vapours and in Solution. John Edward Purvis (T., 1915, **107**, 496—509).—In earlier papers (T., 1913, **103**, 1088, 1638) it has been shown that the absorption spectra of the vapours of the iodoanilines, *p*-iodophenol, the nitrobenzenes and nitrotoluenes, *o*-nitrophenol, *o*-nitroanisole, *o*-nitroaniline, and the nitrobenzaldehydes do not exhibit any of the numerous vapour bands found in benzene, toluene, aniline, phenol, and benzaldehyde (T., 1911, **99**, 811, 1699, 2318), and that the finer vapour bands are eliminated as the number of chlorine or bromine atoms in the nucleus is increased.

Investigations have now been made with other halogen and

various nitrile derivatives of benzene and toluene in order to ascertain the extent to which the absorption is affected: (1) by the introduction in the benzene nucleus of the two dissimilar atoms of chlorine and bromine, as in the *o*-, *m*-, and *p*-chlorobromobenzenes, as compared with the dichloro- and dibromo-benzenes and with benzyl chloride; (2) by the introduction of the nitrile group, as in benzonitrile and the *o*-, *m*-, and *p*-toluonitriles, as compared with phenylacetonitrile; and (3) by the total replacement of the hydrogen atoms in the nucleus, as in hexachlorobenzene and hexamethylbenzene, or by the addition of six atoms of chlorine, as in hexachloro*cyclo*hexane.

The work has led to the following results. Many of the vapour bands in *p*-dichloro- and *p*-dibromo-benzene, in *o*-, *m*-, and *p*-chlorobromobenzene, in benzonitrile, and in *o*-, *m*-, and *p*-toluonitrile, disappear when the substances are in solution, and are replaced by a few, moderately wide, diffuse bands. There are marked differences in the absorption phenomena of the isomeric substances, especially in the para-compounds, as compared with the ortho- and meta-compounds; these differences are more strongly marked in the vapours than in the solutions. Narrow vapour bands are absent in phenylacetonitrile, benzyl chloride, and benzyl alcohol. In hexachloro*cyclo*hexane, hexachlorobenzene, and hexamethylbenzene both vapour bands and solution bands are completely eliminated. The vapour bands and the solution bands resemble one another at the higher temperatures and pressures in those compounds which exhibit a series of finer vapour bands at the lower temperatures and pressures.

These results are discussed from a consideration of the oscillations of different electronic centres. E. G.

Radiometric Measurements of the Ionisation Constants of Indicators. E. J. Shaeffer, M. G. Paulus, and Harry C. Jones (*J. Amer. Chem. Soc.*, 1915, **37**, 776—807).—In connexion with investigations in which the authors are engaged, accurate measurements were required of the hydrolysis constants of certain salts, and the indicator method was considered suitable for the purpose. The ionisation constants of indicators which have hitherto been recorded show wide variations, and the present radiometric investigation was therefore undertaken. Methyl-orange was studied, and a method developed by the application of Beer's law, which readily gave the concentration of the yellow azo-base and that of the red quinoid ion.

The method described, depending on the use of the radiomicrometer and the grating spectroscope, is superior to any method used previously, and serves as well for a two-coloured as for a one-coloured indicator. Very small concentrations of coloured components were determined, and it was found that minute concentrations of hydrogen and hydroxyl ions can be rapidly and accurately estimated by radiometric measurements. Satisfactory constants were obtained for the ionisation of methyl-orange as a base, the value found being $2{\cdot}1 \times 10^{-11}$.

The ionisation and hydrolysis constants found for phenolphthalein, regarded as a monobasic acid, were far from satisfactory. Wegscheider (A., 1908, ii, 806) and Rosenstein (A., 1912, ii, 893) have suggested that it acts as a dibasic acid.

From a knowledge of the ionisation constant of methyl-orange, and by means of radiometric observations, the ionisation constant of a very weak base, aluminium hydroxide, and the hydrolysis constant of aluminium sulphate, have been determined. The method can also be used to determine the ionisation constants of very weak acids and the hydrolysis constants of their salts. E. G.

General Behaviour of Optically Active Compounds as regards the Dependence of Rotation on Temperature, Dilution, Nature of Solvent and Wave-length of Light. T. S. PATTERSON (*Trans. Faraday Soc.*, 1914, **10**, 111—117).—A general discussion of the relations exhibited between the optical rotation and the conditions of temperature, concentration, nature of solvent, and wave-length of light employed in the measurement. Two points are mainly discussed in this connexion: (1) the occurrence and position of the maxima and minima of optical rotation and the influence of the above-mentioned factors; (2) rotation dispersion. In the latter case, after considering the effect of a change in wave-length of the light used on the position of the maximum rotation, the author considers the term abnormal rotation dispersion. It is pointed out that the oft-stated definition, "That rotation dispersion is the ratio of the rotations for various colours of light to the rotation for one given colour," is unsatisfactory, and leads to misleading conceptions, the chief of which being that substances are said to possess an abnormal rotation dispersion, without any real, definite conception being attached to the term normal rotation dispersion. J. F. S.

Optical Rotation and Cryoscopic Behaviour of Sugars Dissolved in (*a*) Formamide, (*b*) Water. JOHN EDWIN MACKENZIE and SUDHAMOY GHOSH (*Proc. Roy. Soc. Edin.*, 1914–15, **35**, 22—45).—The molecular weight of β-*l*-arabinose, *l*-xylose, α-*d*-glucose, α-*d*-galactose, *d*-mannose, *d*-fructose, α-lactose, and β-lactose have been determined in formamide and aqueous solution by the cryoscopic method. The results show that in no case does an association of the sugar molecule occur. The optical rotation of the same sugars were measured at temperatures from 12—20° in both water and formamide solutions, using sodium light. In every case it is shown that mutarotation occurs in non-aqueous solutions with a velocity of the same order, but rather less than that observed in aqueous solutions. This is taken to indicate that the hydrate theory of mutarotation (Lowry, T., 1903, **83**, 1314; Armstrong, T., 1903, **83**, 1305) is untenable. This view is shown to be supported by the results of Grossmann and Bloch (A., 1912, ii, 218) on the mutarotation of sugars in pyridine and formic acid solutions. The values of Grossmann and Bloch for pyridine solutions are inserted in the paper, and shown to be of the same nature as those obtained in formamide solution. J. F. S.

Rotation Dispersion in Homologous Series. AUG. HAGENBACH (*Zeitsch. physikal. Chem.*, 1915, **89**. 570—596).—The specific rotatory powers of homologous series of compounds have been examined with the object of deducing the relations exhibited by the rotatory dispersive power. The compounds in question fall into three groups: (*a*) alkyl and aryl derivatives of methylenecamphor; (*b*) derivatives of citronellal; (*c*) menthol and menthyl esters.

The analysis of the data shows that the ratio of the rotations α'_λ and α_λ for any two members of one of these groups is independent of the wave-length λ. From this it follows that if the relation between the specific rotation α of one of these compounds and the wave-length λ is expressed by the equation $\alpha=f(\lambda)$, the dispersion of the homologous compounds can be represented by the equation $\alpha=Cf(\lambda)$, where C is a constant characteristic of each homologous derivative. The form of the function $f()$ has not been exactly determined, but the data can be approximately represented by the equation $\alpha=A+B/\lambda^2$ or $\alpha=A/\lambda^2+B/\lambda^4$. The specific factor C is related to the constants A and B by the equation $C=\alpha'/\alpha=A'/A=B'/B$, in which α, A, and B and α', A', and B' are corresponding values for two compounds belonging to the homologous series. H. M. D.

Experimental and Theoretical Investigation of Substances showing Anomalous Dispersion of Molecular Rotatory Power. G. BRUHAT (*Ann. Physique*, 1915, [ix], **3**. 232—282).—The anomalous dispersion and circular dichroism which are exhibited by certain coloured solutions have been further investigated by experiments on solutions of substances of relatively simple composition. The substances found to produce these effects include nickel hydrogen tartrate, potassium nickel tartrate, uranyl tartrate, *l*-bornyl dithiourethane, $CSPh{\cdot}NPh{\cdot}CS{\cdot}O{\cdot}C_{10}H_{17}$, and the corresponding compound derived from *d*-borneol. In all cases, the anomalous dispersion is found to be associated with circular dichroism, and can be explained by the presence of an absorption band in the visible region of the spectrum. H. M. D.

Chemical Action of Light. XXX. G. CIAMICIAN and P. SILBER (*Atti R. Accad. Lincei*, 1915 [v], **24**. i, 17—21).—The authors criticise certain of the results obtained by Paternò (this vol., ii, 36). The latter found that, under the influence of light, benzophenone and cymene yield only benzopinacone, but the authors have shown that this product is accompanied by dicymyl (A., 1910, i, 489).

Paternò and Peret (A., 1914, ii, 234) state that the interaction of ethyl alcohol and acetaldehyde leads to no definite result, but the authors find that it yields butylene $\beta\gamma$-glycol,

$$OH{\cdot}CHMe{\cdot}CHMe{\cdot}OH,$$

together with a small proportion of diacetyl.

Claims for priority are also made against Paternò. T. H. P.

Experiments on Radioactive Emanations. A. DEBIERNE (*Ann. Physique*, 1915, [ix], **3**, 18—61).—An account is given of the

preparation of pure radium emanation, and of the investigation of its properties.

The emanation, freed from foreign gases as far as possible by the action of suitable reagents, was subjected to fractional condensation, and the major portion, condensing between $-145°$ and $-165°$, was collected separately. This product is apparently not quite pure, for it exhibits the initial contraction noted by previous observers. In agreement with Ramsay's views, the author's experiments can be interpreted on the assumption that this contraction is associated with the spontaneous elimination of the impurities in the emanation. From a comparison of the γ-ray activity of the resulting pure product with that of radium in radioactive equilibrium, it is found that the volume of emanation in equilibrium with 1 gram of radium is equal to 0·58 cubic mm. After the application of certain corrections, this becomes 0·605 cubic mm., which agrees closely with the values recorded by Rutherford and by Gray and Ramsay (compare T., 1909, **95**, 1073).

The spectrum of the pure emanation has been examined, with results in close agreement with those obtained by Royds (A., 1909, ii, 206, 287). Measurements of the decay constant of the emanation at atmospheric pressure are in accord with the results obtained at low pressures and in mixtures containing foreign gases. No difference could be detected in the constant for fractions of the emanation condensed at different temperatures.

The heat liberated in the decay of radium and of radium emanation has been measured by the use of a Bunsen ice calorimeter. The results indicate that 18—20% of the total heat liberated in the disintegration of radium (in radioactive equilibrium) is to be attributed to the primary formation of the emanation.

H. M. D.

The Atomic Weight of Radioactive Emanations. A. Debierne (*Ann. Physique*, 1915. [ix], **3**. 62—96).—The results obtained in previous measurements of the atomic weight of radium emanation by diffusion methods suggest, on the whole, a much smaller value than that which corresponds with the generally accepted relation between radium and its emanation. Since in these experiments the emanation is admixed with relatively very large quantities of foreign gases, and its partial pressure, in consequence, is extremely small, it seemed possible that the ordinary relation between the density and the rate of diffusion might not hold under these conditions.

In order to test this, experiments have been made in which the rate of passage of gases through a small hole in a thin sheet of platinum was measured, when the pressure on one side was only a small fraction of a mm., whilst on the other side of the aperture the pressure was maintained as low as possible by means of a continuously acting Gaede pump. Observations were made with oxygen, carbon dioxide, sulphur dioxide, and argon at pressures varying from 0·075 mm. to 0·001 mm. The results obtained show that the relation between the initial pressure p_0 and the pressure

p at the end of time t is given by the relation $p = p_0 e^{-\mu t}$, in which μ is a coefficient which is proportional to the rate of flow of the gas through the pin-hole. In accordance with this equation, a straight line is obtained when $\log p$ is plotted as a function of t. The slope of this line is a measure of the coefficient μ, and the experimental data show that $M\mu^2$, where M is the molecular weight, has the same value for each of the four gases examined.

Experiments were also made with mixtures of oxygen and sulphur dioxide, and in this case it was found that the pressure p of the mixture after time t is related to the initial pressure p_0 by the equation

$$p = p' + p'' = p_0(a/1 + a \cdot e^{-\mu' t} + 1/1 + a \cdot e^{-\mu'' t}),$$

in which p' and p'_0 are the partial pressures of oxygen, and p'' and p''_0 those of sulphur dioxide, and a is the ratio of the initial pressures p'_0/p''_0. It follows from this result that each gas acts independently of the other.

These results afford an experimental basis for the application of the Bunsen method to the determination of the atomic weight of the emanation, and the same apparatus has been used for this purpose. From a comparison of the straight lines obtained with radium emanation and oxygen, the ratio of the densities is found to be 6·9, which gives 221 ± 2 for the atomic weight of the emanation.

On account of the greater rate of decay of thorium emanation, the experimental method requires some modification, but not in any essential way. The observed results give a number of the order of 200 for the atomic weight, but the accuracy attainable is not very great. H. M. D.

The Electron Emission of the Calcium Oxide Electrode in a Vacuum. WERNER GERMERSHAUSEN (*Physikal. Zeitsch.*, 1915, **16**, 104—108).—The behaviour of the calcium oxide electrode has been investigated in the highest possible vacuum at various temperatures up to 1400°. In opposition to the theory (compare Fredenhagen, A., 1913, ii, 903; Gehrts, A., 1913, ii, 1005) that the activity of the electrode depends on the dissociation of the calcium oxide, the results obtained by the author indicate that the activity of the electrode is due to a specific electronic emission on the part of the oxide. The presence of traces of residual gases in the discharge tube diminishes the effect to a very considerable extent, as in the case of the emission from tungsten investigated by Langmuir (A., 1914, ii, 412). When the residual gases are removed, the intensity of the electron emission increases, and at a given temperature the effect remains constant and independent of the length of time during which the discharge is passed. For small differences of potential, the emission is nearly independent of the temperature between 1000° and 1400°. The equation for the limiting value of the current in the absence of traces of foreign gases, which was found by Langmuir (*loc. cit.*) to represent the experimental observations made with tungsten, is also found to yield satisfactory results in the case of the calcium oxide electrode. H. M. D.

Adsorption Experiments with Radioactive Elements. KARL HOROVITZ and FRITZ PANETH (*Zeitsch. physikal. Chem.*, 1915, **89**, 513—528).—The adsorption of radium, polonium, thorium-*B*, and thorium-*C* by various substances has been investigated with the object of ascertaining whether there is any connexion between the adsorption and the solubility of the radioactive substances. The adsorbents used were barium sulphate, barium chromate, cupric oxide, chromic oxide, titanium dioxide, tantalic oxide, manganese dioxide, silver chloride and bromide (insolated and non-insolated). These were shaken for ten minutes with the radioactive solution, and the influence of acid or alkali on the adsorption was determined in parallel experiments with the addition of varying quantities of these reagents to the solution.

The results obtained show the existence of a connexion between the magnitude of the adsorption and the solubility of the "analogous" radioactive compound. By the "analogous" compound is meant the compound of the radioactive element which contains the same electronegative constituent as the adsorbent. Those radioactive elements are adsorbed by a given adsorbent, for which the "analogous" compounds are relatively insoluble. In accordance with this relation, it is found that the adsorption increases when an acid which has the same anion as the adsorbent is added to the radioactive solution. The addition of sulphuric acid increases the adsorption exhibited by barium sulphate, hydrochloric acid that shown by silver chloride, and the addition of nitric acid is also found to increase the adsorption effect in the case of the various metallic oxides. This influence of the common ion on the adsorption is attributed to the reduction in the solubility of the "analogous" radioactive compound. H. M. D.

Distribution of Radio-elements in Rocks. II. Spring Deposits. G. WEISSENBERGER (*Centr. Min.*, 1914, 481—490. Compare A., 1914, ii, 608).—The ochre deposited by a strongly radioactive chalybeate spring in the Villnösser Ravine, Tyrol (A., 1913, ii, 1012), was examined. The rock from which the water issues is a graphite-quartzite containing a small amount of zircon. Analyses are given of this rock (SiO_2 91·41, C 1·56%, etc.), and of samples of the ochre collected at different spots (Fe_2O_3 62·82—67·26, loss on ignition 20·81—25·45, SiO_2 7·84—9·82, Mn_3O_4 1·24—1·47%, etc.). The amount of radium in the rock is $2·73 \times 10^{-10}$, and in the ochre $7·95 \times 10^{-9}$—$1·58 \times 10^{-9}$%, being greater in amount in the samples collected nearer the point of issue of the spring. Thorium in the rock $1·16 \times 10^{-3}$, and in the ochre $8·11 \times 10^{-4}$—$3·56 \times 10^{-3}$%. L. J. S.

The Radioactive Content of Certain Minnesota Soils. JAMES C. SANDERSON (*Amer. J. Sci.*, 1915, [iv], **39**, 391—397).—A method has been devised by which the radium content of a soil may be determined in a sample of about 50 pounds in weight. This has been applied to the investigation of the radium content of thirteen typical Minnesota soils, in which the content of thorium was also

measured. The radium content in these varies from 17 to 80×10^{-14} gram per c.c., and that of thorium from 25 to 71×10^{-7} gram per c.c. There is no apparent connexion between the two series of numbers.

The soils examined can be classified in two groups according to their fertility, and without exception it is found that the soils belonging to the fertile group are richer in radioactive emanations than soils falling into the less fertile group. This agrees with the results which have been obtained in experiments on the change in the fertility of soils when treated with water containing radium emanation. H. M. D.

Degree and Character of the Radioactivity of the Kuvaka Spring of the Nishnelomovski District of the Penzenski Government. P. P. von Weimarn (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 742—745).—The water of this spring exhibits feeble radioactivity, which increases in intensity as the yield of the spring diminishes. Since the radioactivity rapidly vanishes when the water is kept, it is due only to dissolved emanation. T. H. P.

Cause of the Electrical Conductivity of Air which has been in Contact with Phosphorus. II. Rudolf Schenck and E. Breuning (*Ber.*, 1914, **47**, 2601—2611. Compare Schenck, Mihr and Banthien, A., 1906, ii, 326).—In the previous communication it has been shown that the ionisation of air which has been in contact with phosphorus is due to the interaction of phosphorus trioxide and water. By the use of a special apparatus, of which a diagrammatic representation is given, experiments have been made to decide whether the cause of the ionisation is the mere occurrence of chemical reaction between the phosphorus trioxide and water, or whether some product of the reaction is the agent. On allowing water vapour and phosphorus trioxide to react in a current of nitrogen, and passing the gas through a vessel cooled in liquid air, it is found that the issuing gas has lost all sign of ionisation; if the temperature of the cooled vessel is allowed to rise, ionisation manifests itself strongly. The ionisation is therefore due to a reaction product, a "*phosphorus emanation*," which undergoes complete condensation at $-180°$, but has an appreciable vapour pressure at $-80°$. Nothing is at present known as to the nature and composition of this active substance.

D. F. T.

The Electrical Conductivity of Colloidal Solutions. Harald Nordenson (*Kolloid Zeitsch.*, 1915, **16**, 65—69).—According to measurements of the velocity with which colloidal particles move in an electric field, it would seem that the mobility is of the same order of magnitude as that of the ions. On the assumption that Stokes' law is applicable to the motion of the colloid particles and the ions, it is shown that the maximum electric charge of a colloidal or suspended particle is proportional to its radius. It is shown, further, that if the same quantity of a substance, for example, a

metal, is present (*a*) in the form of colloidal particles, (*b*) in the form of ions, the conductivity due to this substance will vary inversely as the square of the radii. According to this relation, it is possible to calculate the conductivity of a colloid in terms of the concentration and the degree of dispersity. The values obtained in this way show that the conductivity of colloids of average dispersity is negligibly small. It follows from this that the relatively high values for the conductivity of colloids, which have been recorded by a number of observers, are in all probability due to the presence of small quantities of electrolytes.

In the case of concentrated solutions of highly dispersive colloids, in particular solutions of non-metallic colloids, it is possible that an appreciable proportion of the observed conductivity may be attributed to the colloidal substance itself, but even in these cases the major portion of the conductivity is with great probability to be debited to the presence of adsorbed electrolytes.

H. M. D.

Dielectric Constant of Liquid Hydrogen Iodide. Herman Schlundt and Julius Underwood (*J. Physical Chem.*, 1915, **19**, 338. Compare Schaefer and Schlundt, A., 1910, ii, 12).—A redetermination of the dielectric constant of hydrogen iodide has given 2·65 at 19° and 3·61 at −50° for the liquid substance, and 3·05 at −70° for the solid. The values recorded previously (*loc. cit.*) seemed to show anomalous behaviour on the part of hydrogen iodide, but the new values show relations of the kind exhibited by other substances.

H. M. D.

Potentiometric Arrangement for Electrochemical Investigations. O. Scarpa (*Ann. Chim. Applicata*, 1915, **3**, 157—161).—The author describes a simple and inexpensive potentiometer constructed of the ordinary apparatus of a physico-chemical laboratory, and capable of reading from 0·0001 volt to 10 volts.

T. H. P.

Influence of Organic Bases on the Potential of the Hydrogen Electrode. Arrigo Mazzucchelli (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 139—143).—The author has found recently (*ibid.*, 1914, [v], **23**, ii, 503) that addition of salts of various organic bases exerts an appreciable influence on the potential of a zinc electrode immersed in zinc sulphate solution. Similar investigations with the hydrogen electrode show that this also is rendered more "noble" by the presence of an organic base. Effects of varying magnitude are observed with quinine and cinchonine hydrogen sulphates, and brucine, veratrine, coniine, hydrastine, quinoline, lutidine, dimethylaniline and phenylhydrazine sulphates, but, of the simpler bases, quinoline and dimethylaniline exert the greatest action, just as is the case with the zinc electrode. The effect produced by phenylhydrazine is exceptionally large, and may be due to true chemical depolarisation. Just as with zinc, the initial, energetic action of these bases diminishes more or less rapidly. The effects due to starch, gelatin, and saponin are negligibly small.

Since, in the absorption of salts by solid surfaces, the basic portion is often absorbed in the larger amount, it may be that the same happens in this case. T. H. P.

Properties of Silver Iodide Interpreted in Relation to Recent Thermodynamic Conceptions. GRINNELL JONES and MINER LOUIS HARTMANN (*J. Amer. Chem. Soc.*, 1915, **37**, 752—775).—Jones (A., 1909, ii, 210) has proposed an explanation of the negative coefficient of expansion of silver iodide. From a study of the free energy of formation of this salt, it has been found that, as the temperature rises, the mutual affinity of silver and iodine increases their tendency to produce a diminution in volume. As the data employed in these calculations were obtained from various sources, and the errors of all of them entered into the result, it was considered desirable to test this explanation of the negative coefficient of expansion by direct measurements at two temperatures of the potential of an electrolytic cell which produces silver iodide from its elements.

Measurements have been made of the *E.M.F.* of silver–silver iodide–iodine cells at 0° and 25°. The construction of these cells is described, and an improved method has been devised for preparing silver–silver iodide electrodes. From the results, the free energy of formation of silver iodide from silver and iodine has been found to be 65·1 kilojoules at 0° and 66·1 kilojoules at 25°. The conclusion that the mutual affinity of silver and iodine increases with rising temperature is thus confirmed.

The heat of formation of silver iodide is 61·0 kilojoules.

It is shown that the relationship between the properties and thermodynamic constants of silver iodide support many of the conclusions drawn by Richards from his hypothesis of compressible atoms, but do not support the so-called Nernst heat theorem. E. G.

Complications at the Anode in the Silver Coulometer (Voltameter). T. W. RICHARDS and F. O. ANDEREGG (*J. Amer. Chem. Soc.*, 1915, **37**, 675—693).—In an earlier paper (this vol., ii, 81) an account was given of the occurrence of included electrolyte in the cathode deposit in the silver coulometer. It has been found by Richards, Collins, and Heimrod (A., 1900, ii, 256) that the older form of voltameter, containing filter-paper, caused a heavier deposit than that in which the anode liquid is kept away from the cathode by means of a porous cup. A further study of this question has confirmed the view (Richards and Heimrod, A., 1902, ii, 592) that, even in the absence of filter-paper, the anode liquid may cause an increase in the weight of the ignited cathode deposit, and this effect is attributed to metastably dissolved silver in the form of an argentous ion. The Kohlrausch coulometer, whilst giving better results than the filter-paper form, does not entirely obviate the difficulty. The best results were obtained by means of a small, porous cup coulometer with a highly burnished cathode and pure electrolyte, the deposit being ignited at incipient redness. E. G.

Electrolytic Phenomena at Diaphragms. II. The Dependence of the Magnitude and Direction of the Changes in Concentration and of the Transport of Water on the Hydrogen Ion Concentration. ALBRECHT BETHE and THEODOR TOROPOV (*Zeitsch. physikal. Chem.*, 1915, **89**, 597—637. Compare this vol., ii, 213).—Further experiments have been made in order to ascertain the influence of the hydrogen ion concentration on the changes which occur in the composition of salt solutions in the immediate neighbourhood of an interposed diaphragm when a current is passed through the salt solution. Salt solutions containing varying amounts of acid were examined, and, after the passage of a measured quantity of electricity, samples of solution from the positive and negative sides of the diaphragm were analysed. The anion concentration was estimated by a suitable chemical method, and the hydrogen ion concentration electrometrically by means of a hydrogen electrode. The change in volume of the anode solution was determined with the aid of a capillary tube communicating with the anode chamber of the electrolytic apparatus.

From the results obtained with a number of diaphragms, it is evident that the magnitude of the change of concentration and the transport of water is dependent on the hydrogen ion concentration of the original solution. With diaphragms of collodion, wood, and charcoal the concentration always increases on the cathode side of the diaphragm, and water is always transported in the direction of the positive current, whatever the hydrogen ion concentration may be. On the other hand, with diaphragms of gelatin, egg albumin, pig's bladder, and gypsum, the effect depends on the hydrogen ion concentration. When this exceeds a certain value, the electrolyte increases in concentration on the anode side, and the water transport follows the direction of the negative current. The hydrogen ion concentration corresponding with the reversal of these effects depends on the nature of the ions. According to the results obtained with differently concentrated sodium chloride solutions, it appears that the hydrogen ion concentration at which the above changes are reversed (isoelectric point) increases with increasing salt concentration. When referred to the same quantity of electricity, the magnitude of the change in the concentration decreases with increasing strength of the solution.

With jelly diaphragms containing varying amounts of gelatin, the concentration changes increase with the gelatin content of the diaphragm.

The phenomena described are supposed to be connected with the adsorption of the cations or anions by the walls of the porous diaphragm, which gives rise to changes in the relative mobility. The direction of the water transference is determined essentially by that of the relatively mobile ions which are not adsorbed by the diaphragm. The degree of hydration of the ions is consequently of considerable importance in regard to the magnitude of the diaphragm effects. H. M. D.

The Hydrate Problem. I. Calculation of the Quantity of Water Enveloping the Ions from the Electrolytic Mobilities. HEINRICH REMY (*Zeitsch. physikal. Chem.*, 1915, **89**, 467—488).—The author discusses the transference of water by the ions in the passage of a current through an aqueous solution of an electrolyte, and its bearing on the question of the formation of hydrated ions.

Attempts have been made by earlier observers to determine the quantity of water transferred by a comparison of the Hittorf and the "true" transport numbers, but it is shown that no method is yet available for the derivation of "true" transport numbers which can be regarded as trustworthy. The method used by Riesenfeld and Reinhold (A., 1909, ii, 540) for the determination of the water transfer involves the assumption that the "true" transport numbers are constant in dilute solution (less than $0{\cdot}1N$). In the case of potassium chloride, it leads to values for the water transfer which vary in the ratio 1 : 28 when the concentration of the salt is increased from $0{\cdot}01N$ to $1N$, and this is regarded as an improbable result.

A new method of calculating the size of the water envelope is proposed which depends on the application of Stokes' formula to the ionic mobilities. From this formula, the radius R of the ion may be obtained in terms of the radius of the hydrogen ion, which is assumed to have no water envelope. On comparing the radius R with that calculated from the atomic volume, it is found that the difference $R-r$ is nearly equal to the diameter of a water molecule in the case of a considerable number of univalent positive and negative ions. In other words, if r_w is the radius of a water molecule, $(R-r)/2r_w$ is approximately equal to unity. For other univalent ions, this ratio has a higher value—$Ag^{\cdot}$ 1·5, $Na^{\cdot}$ 1·9, $Li^{\cdot}$ 2·6, ClO'_3 1·5. Bivalent ions also gave a value greater than unity.

The value $(R-r)/2r_w=1$ is supposed to indicate that the ions are surrounded by a single layer of closely packed water molecules. Values greater than unity indicate a greater degree of hydration, but a departure from the assumed spherical form may also influence the result. In the case of the OH' ion, the method indicates that the ion combines with a single molecule of water.

The number of water molecules in the envelope of other ions is as follows: $H^{\cdot}$ 0, $Cs^{\cdot}$ 13, $Rb^{\cdot}$ 14, $K^{\cdot}$ 16, $NH_4^{\cdot}$ 17, $Na^{\cdot}$ <66, $Li^{\cdot}$ <120, $Tl^{\cdot}$ 16, $Ag^{\cdot}$ 29, I' 15, Br' 15, Cl' 16, ClO_4' 17, ClO_3' 26, NO_3' 19, CNS' 25. These are compared with the numbers obtained by Riesenfeld and Reinhold (*loc. cit.*). H. M. D.

The Hydrate Problem. II. A New Method for the Determination of the Electrolytic Transport of Water. HEINRICH REMY (*Zeitsch. physikal. Chem.*, 1915, **89**, 529—569. Compare preceding abstract).—An attempt has been made to determine the quantity of water which is carried by the ions by a method in which the changes in volume of the anode and cathode solutions are subjected to direct measurement. This method has been applied to solutions of various chlorides which were electrolysed

between a silver anode and a silver chloride cathode. In order to fix the middle portion of the solution, the anode and cathode tubes were connected by means of a two-necked bottle containing solution which had been transformed into a solid jelly by the addition of gelatin. Capillary tubes communicating with the anode and cathode chambers enabled the changes in volume to be read off directly.

The observed changes in volume require to be corrected for the electro-endosmotic transport of water, and it is assumed that the specific electroendosmose is practically independent of the concentration of the salt solution. The corrected values of the water transport are then used for the calculation of the degree of hydration of the ions on the assumption that the transport numbers for the solid jelly are not appreciably different from the corresponding numbers for the aqueous solution. The hydration numbers are relative, and those actually recorded are derived by assuming that the number of mols. of water transported by the chlorine ion lies between six and ten. Corresponding with the limiting values Cl' 6 (10), the hydration numbers obtained are as follows: Br' 5·0 (9·2), $K^{\cdot}$ 7·4 (11·6), $Na^{\cdot}$ 11·9 (18·4), $Li^{\cdot}$ 16·3 (27·1), $Ba^{\cdot\cdot}$ 2·3 (17·0), $Ca^{\cdot\cdot}$ 9·4 (28·1). These numbers have reference to solutions the concentration of which lies between 0·5 and 1·5*N*. The errors of experiment are greater in the case of more dilute solutions. It is to be noted that the hydration numbers for the alkali metal ions are in close agreement with the values obtained by Washburn (A., 1909, ii, 1009), who employed an entirely different method, involving the use of a non-transportable reference substance as a measure of the transfer of water. The agreement between the two sets of values is considered to furnish strong evidence in favour of the view that the electrolytic ions in aqueous solution are hydrated. H. M. D.

Ionic Hydration and Transference Numbers of Cæsium Chloride. Edward W. Washburn and Earl B. Millard (*J. Amer. Chem. Soc.*, 1915, **37**, 694—699).—Washburn (A., 1908, ii, 1009) has given an account of a study of the transference numbers and relative ionic hydrations of the chlorides of lithium, sodium, and potassium in aqueous solution at 25°. The measurements were made by transference experiments in the presence of a suitable non-electrolyte as a reference substance. The investigation has now been extended to cæsium chloride.

Transference experiments in presence of raffinose as the reference substance have shown that the true transference number of the cæsium ion in 1·2*M* cæsium chloride solution at 25° is 0·491, and the water transference 0·33±0·06 formula weights of H_2O per faraday from anode to cathode. Cæsium chloride is the least hydrated of the alkali ions, and, on the average, carries 0·65 mol. less water than the potassium ion. Similar experiments with potassium nitrate showed that in this case, also, the water transference is from anode to cathode.

The addition of cæsium chloride to a raffinose solution increases

its specific rotatory power to the same extent as does potassium chloride.

Bailey's statement (T., 1894, **65**, 445) that cæsium chloride is volatile with steam could not be confirmed. E. G.

Influence of an Alternating Current on Electrolysis by a Direct Current. II. JNANENDRA CHANDRA GHOSH (*J. Amer. Chem. Soc.*, 1915, **37**, 733—752).—In an earlier paper (A., 1914, ii, 838) an account was given of the action of an alternating current of high frequency on simple voltaic cells. The investigation has now been extended to a study of the influence of an alternating current on electrolytic cells.

It has been found that in perfectly reversible cells the alternating current has no action when impressed on the cell, together with a direct current. If the electrolytic cell is irreversible, the alternating current produces a great increase in the current strength through the circuit, owing to a diminution in the back *E.M.F.* of polarisation. A diminution in the discharge potential also occurs in electrolytic cells consisting of two cathodes and two anodes, when the alternating current is caused to act between the anodes or the cathodes, but is not allowed to pass through the whole circuit.

These results indicate that the alternating current acts primarily on the surfaces of the electrodes, and it is suggested that, in some way, it causes an alteration in the nature of the surfaces. Newbury (T., 1914, **105**, 2431) considers that the ions penetrate into the interior of the electrodes, and that the molecules produced by their discharge break the surface in making their escape. It can be readily imagined that an alternating current of high intensity would reduce the mechanical resistance offered to the passage of the molecules out of the electrode surface, and thus facilitate the liberation of the ions and effect a decrease of the discharge potential. E. G.

Electrolytic Deposition of Zinc at the Surface of the Solution. A. A. TITOV and S. M. LEVI (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 909—934).—The authors have investigated the phenomenon studied by Mylius and Fromm (A., 1894, ii, 267) and by Freundlich and Novikov (A., 1910, ii, 577), according to whom, electrolysis of a zinc solution, the surface of which is covered with oil, leads to the separation of a superficial film of the metal. It is found that this film-formation occurs on electrolysis, not only of zinc sulphate solution, but also of solutions of the chloride and acetate, provided these are sufficiently acidified. The phenomenon is favoured by a low concentration of hydrogen ions, but increase of the latter results eventually in hindrance, or even prevention, of the growth of the film. The formation of the film is retarded by the appearance of spongy zinc, and all measures taken to prevent the deposition of the metal in this form are advantageous. The best films are obtained when the zinc is precipitated in a bright, finely crystalline condition, a coarsely crystalline or dark

deposit opposing the formation of films. The latter are obtained within wide limits of variation of the current density and of the concentration of the solution, and the lower the concentration the lower the permissible current density. With constant voltage, the current density remains more or less constant during the deposition of the film only at the periphery of the latter, and diminishes rapidly at the lower surface. T. H. P.

Mechanism of the Chemical Action of Electric Discharges. The Rôle of Ionisation. E. Briner (*J. Chim. Phys.*, 1915, **13**, 18—32. Compare this vol., ii, 6).—Further observations have been made on the stationary state which is ultimately attained when an arc discharge is passed through a mixture of nitrogen and hydrogen. The final condition of the gas is the same, whether the discharge is passed through ammonia or through a mixture of the elementary gases in the ratio $N_2 : 3H_2$.

From a series of experiments, in which an auxiliary electrode was introduced into the discharge chamber, and by means of which the electrical conditions in the neighbourhood of the arc were varied as widely as possible, it has been found that the stationary state is not appreciably affected by these changes. From this, the conclusion is drawn that the chemical reaction is not due to ions formed under the influence of the ultra-violet radiation from the arc. The facts suggest, on the other hand, that the chemical change is a purely thermal effect, and it is supposed that the ammonia is formed from monatomic nitrogen and hydrogen molecules. Assuming that $2H = H_2 + 130$ Cal., and $2N = N_2 + 150$ Cal., it follows that $N + 3H = NH_3 + 300$ Cal.

The formation of nitric oxide on the passage of the discharge through a mixture of nitrogen and oxygen has also been found to be independent of the electrical conditions, and in this case the reacting components are also supposed to be the thermally dissociated atoms. H. M. D.

[A Relation between the Specific Heat (c), the Linear Coefficient of Expansion (β), the Density (δ) and the Elastic Modulus (E) of the Solid Elements.] Johann Kleiber (*Ann Physik*, 1915, [iv], **46**, 1054—1056).—From the data for lead, gold, tin, silver, platinum, tantalum, copper, nickel, magnesium, aluminium, and iron it is found that the velocity of sound in these elements is a linear function of $\sqrt{c/\beta}$, and can be represented by the equation $v = 57{\cdot}698\sqrt{c/\beta} - 637$. From $v = 99{\cdot}04\sqrt{E/\delta}$, it follows that c, β, δ, and E are connected by the equation

$$99{\cdot}04\sqrt{E/\delta} = 57{\cdot}698\sqrt{c/\beta} - 637.$$

When three of the quantities in question are known, this equation may be utilised for the determination of the fourth. H. M. D.

A Simple Apparatus for Determining the Melting Point of Substances which are Bad Conductors of Electricity. Ignacio González Marti (*Anal. Fis. Quim.*, 1915, **13**, 160—162).—A descrip-

tion of a form of melting-point apparatus in which the heat is generated by the electric resistance of the substance under examination. A. J. W.

Influence of Temperature and Solvent on the Molecular Weight of Dissolved Substances. ERNST BECKMANN and MARIA MAXIM (*Zeitsch. physikal. Chem.*, 1915, **89**, 411—416).—The influence of temperature on the molecular weight of phenol in carbon tetrachloride has been examined by boiling-point measurements at 75°, 66°, and 54°, and also by freezing-point measurements at −23°. The boiling-point observations show that the molecular weight increases with increasing concentration, but that the above difference of temperature has no appreciable influence on the molecular weight at a given concentration. For a 2% solution, the value of the association factor changes from 1·34 to 1·31 between 75° and 54°. The association factor is not appreciably altered when the volatilisation of the phenol is allowed for. The freezing-point data give values for the molecular weight which increase from 90 in a 0·019% solution to 313 in a 2·31% solution. The degree of association of the phenol is therefore much greater at −23° than at 54—75°.

A further series of freezing-point measurements was made with bromoform, m. p. 8°. The molecular-weight values increase from 97 in 0·296% solution to 190 in 4·33% solution. The association in bromoform is therefore less than in carbon tetrachloride.

H. M. D.

Vapour Pressure of Halogen Hydrides and Hydrogen Sulphide. O. MAASS and D. MCINTOSH (*Trans. Roy. Soc. Canada*, 1914, [iii], **8**, 65—72).—The vapour pressures of hydrogen bromide, chloride, iodide, and sulphide have been determined at temperatures between their melting points and boiling points. The measurements were made by means of a spiral glass manometer, capable of giving values to 0·08 mm. mercury; the temperatures were obtained in a Dewar vessel filled with ether and solid carbon dioxide, by varying the pressure, and measured by a Travers' hydrogen thermometer. Values are given for hydrogen chloride between −112·5° and −83·6°, for hydrogen bromide between −114·4° and −66·6°, for hydrogen sulphide between −110·0° and −58·1°, and for hydrogen iodide between −106·9° and −34·3°. In all cases except that of hydrogen chloride, the values will be seen to have been determined at temperatures considerably below the freezing point; the vapour-pressure curves, however, show no great change in curvature on passing through the melting point. The following values are found for the melting points and boiling points: hydrogen chloride, m. p. −111·4°, b. p. −83·4°; hydrogen bromide, m. p. −88·1°, b. p. −67·1°; hydrogen sulphide, m. p. −83·6°, b. p. −60·0°; and hydrogen iodide, m. p. −50·9°, b. p. −35·5°. These results are the mean values of four determinations. The latent heat of vaporisation is calculated from the dP/dT values by means of the Clausius equation, and the values

obtained are: hydrogen chloride, $14{\cdot}8 \times 10^{10}$ ergs.; hydrogen bromide, $18{\cdot}7 \times 10^{10}$ ergs.; hydrogen iodide, $21{\cdot}6 \times 10^{10}$ ergs.; and hydrogen sulphide, $19{\cdot}5 \times 10^{10}$ ergs. These values agree well with the experimental values of Elliot and McIntosh (A., 1908, ii, 354).

J. F. S.

Molecular Attraction. XI. New Relations Revealed by Diagraming Internal Pressure as a Negative Pressure. J. E. Mills (*J. Physical Chem.*, 1915, **19**, 257—274. Compare A., 1914, ii, 248, and previous papers).—Four methods for calculating the internal pressure of fluids are described, which are based on the Clausius-Clapeyron equation, on Mills', Dieterici's, and van der Waals' equation respectively. The relations involved are expressed by the equations $p = TdP/dT - P = 31414\mu'/3V^{\frac{2}{3}}_c = CRT/V_c = a$, in which p is the internal pressure, P the total pressure at temperature T, μ' the constant in the equation $\lambda/(d^{\frac{1}{3}} - D^{\frac{1}{3}}) = \mu'$. L, where λ is the internal heat of vaporisation, d the density of liquid, and D that of the saturated vapour, V_c the specific volume of saturated vapour, C a constant, and a the van der Waals' constant. From the available data for *iso*pentane, these equations give the following values for the internal pressure at the critical temperature: 149,635, 159,500, 157,700, and 159,924. It is tolerably certain that the first value is too low, and the divergence is to be attributed to the fact that there is no accurate method for the determination of dP/dT at the critical temperature. If dP/dT is calculated from the empirical equation $dP/dT = 2R/V_c$, the value obtained for p from the equation $p = TdP/dT - P$ is equal to 161,800.

A method of graphing the pressure-volume relations is described which affords a means of depicting the negative internal pressures.

H. M. D.

Influence of Temperature on the Thermal Tonality of Certain Reactions. J. W. Melior (*J. Chim. Phys.*, 1915, **13**, 52—54).—In agreement with the views expressed by Briner (A., 1914, ii, 429), the author considers that a change in the sign of the heat of formation of a compound may be expected when a rise of temperature causes a diminution in the complexity of the molecules of the component elements. H. M. D.

Calorimetric Bomb and the Heat of Combustion of Benzoic Acid. V. Sventoslavski and M. Popov (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 935—975).—In order to obtain uniformity of the values of the heats of combustion of organic compounds, all investigators should carry out their measurements under similar conditions. The constant of the calorimetric system should be determined by the combustion of a single standard substance, benzoic acid being suitable for this purpose (compare Fischer and Wrede, A., 1904, ii, 468; 1908, ii, 155), and all other determinations should be made under the conditions employed in measuring this constant. The most trustworthy values for the number of calories generated in the combustion of 1 gram of benzoic acid at 17° and at constant

volume are: Fischer and Wrede, 6321·3; Berthelot, and Luginin, 6306; the authors, 6310.

Of the various methods which have been devised for determining the water equivalent of the calorimetric system, that given by Stohmann, Kleber and Langbein (A., 1889, 929) is the only one yielding accurate results. The authors have employed the following new method in their work with the bomb calorimeter. Equal weights of the same substance are burned in the bomb in each of two calorimeters, differing considerably in volume. It is then possible to obtain an equation which gives the total water equivalent, but does not contain the heat of combustion of the substance. The accuracy of the authors' measurements of the heat of combustion of benzoic acid, in which a mercury thermometer was employed, is ±0·030—±0·025%, this being at least equal to that of the measurements of Fischer and Wrede, who used a more accurate platinum electric thermometer. The various corrections to be applied to the numerical results are discussed. T. H. P.

Higher Valencies in Oxygenated Organic Compounds. VI. Basic Properties of Oxygen in Ethers. V. V. Tschelincev [with L. K. Belskoi-Smorodinceva, V. K. Perschke and V. A. Pavlov] (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 889—895).—Measurements have been made of the amounts of heat developed by the interaction of the compound PrOMgI with a number of different ethers (compare A., 1914, ii, 171, 172). With diethyl ether, 5·05 Cal. are generated, but with phenyl methyl ether, phenyl ethyl ether, α-naphthyl ethyl ether, β-naphthyl ethyl ether, and diphenyl ether, no heat effect is observed; the suppression of the higher valency in these ethers is ascribed to the negative influence of the acidic phenyl groups (compare A., 1913, ii, 925). Benzyl ethyl ether gives 4·19, diphenylmethyl ethyl ether 2·04, dibenzyl ether 1·57, and triphenylmethyl ethyl ether 0 Cal.

Comparison of these results with those previously obtained with alcohols and phenols shows that the manifestation of higher valencies in ethers is, in general, feebler than in compounds containing hydroxyl groups. The effect of the phenyl group, and of its proximity to the etheric oxygen atom, is shown by the two series: Et_2O 5·05, $CH_2Ph{\cdot}OEt$ 4·19, and $Ph{\cdot}OEt$ 0 Cal.; and $CH_2Ph{\cdot}OEt$ 4·19, $CHPh_2{\cdot}OEt$ 2·04, and $CPh_3{\cdot}OEt$ 0 Cal.

The extent to which the higher valency of the oxygen atom is exerted thus diminishes in the series H·O·H, R·O·H, R·O·R.

T. H. P.

Heat of Neutralisation of Hydroxylamine and Tetramethylammonium Hydroxide. Emil O. Ellingson (*J. Amer. Chem. Soc.*, 1915, **37**, 699—709).—An account is given of determinations by the adiabatic method of the heat of neutralisation of hydroxylamine and tetramethylammonium hydroxide when neutralised with hydrochloric, sulphuric, and trichloroacetic acids in aqueous solutions. The method employed was practically the same as that used by Richards and Rowe (A., 1908, ii, 806), and the adiabatic bath

was similar to that devised by Richards and Jesse (A., 1910, ii, 269) and Richards and Burgess (A., 1910, ii, 391). The concentration of the solutions approximated in some cases to 1 mol. of the reagent to 50 of water, and in others to 1 mol. to 200 of water. The following results were obtained.

For hydroxylamine and hydrochloric acid, concentration 1 : 50, 9483 cal., and concentration 1 : 200, 9292 cal.; for hydroxylamine and sulphuric acid, concentration 1 : 50, 11,445 cal., and concentration 1 : 200, 11,071 cal.; for hydroxylamine and trichloroacetic acid, concentration 1 : 100, 9681 cal., and concentration 1 : 200, 9280 cal. For tetramethylammonium hydroxide and hydrochloric acid, concentration 1 : 200, 12,637 cal; for tetramethylammonium hydroxide and sulphuric acid, concentration 1 : 200, 14,431 cal.; and for tetramethylammonium hydroxide and trichloroacetic acid, concentration 1 : 200, 12,617 cal.

The results for hydroxylamine are from about 0·3% to 2·6% higher, and for tetramethylammonium hydroxide about 7·5% lower, than the values obtained by Thomsen for these bases. The heats of neutralisation with trichloroacetic acid have not been previously determined. E. G.

The Velocity of the Adsorption Reversal. H. Freundlich and E. Hase (*Zeitsch. physikal. Chem.*, 1915, **89**, 417—463).—Further experiments have been made on the reversed adsorption which is exhibited by coagulated mercuric sulphide (compare Freundlich and Schucht, A., 1914, ii, 39). No more suitable coagulating electrolytes than new-magenta and auramine have been found, although many others have been submitted to examination. Other coagulated sols have also been investigated, but coagulated sulphur is the only one found to be suitable, and in this case new-magenta was used as coagulator.

The reversed adsorption is in all cases an auto-catalytic process, the velocity of which in the experiments with mercuric sulphide can be represented by $dx/dt=2k_2t(1+b_2x)(1-x)$ or

$$dx/dt=2k_3t(1+b_3x)(1-x)^2,$$

and in those with sulphur by $dx/dt=k_1(1+b_1x)(1-x)$, in which k_1, k_2, k_3, b_1, b_2, b_3 are constants, and x the increase in concentration of the dye. Corresponding with this difference in the nature of the auto-catalytic reactions, it was found that the flakes of sulphur showed a greater tendency to assume a crystalline form during the progress of the change.

The concentration of the dye has an enormous influence on the velocity of the change. The relation between the velocity-coefficient k and the quantity of adsorbed dye a is given by the equation $k=\kappa . a^p$, in which κ and p are constants, and the value of p varies from 2 to 7. Protective colloids, such as saponin, retard the reversed adsorption when present in small amounts. As in the case of mercuric sulphide, the observations with sulphur show that the velocity increases very rapidly with rise of temperature. The value of A in the Arrhenius formula

$$\log k=-A/T+B$$

is about 15,000, in accordance with which the velocity is quintupled by a rise of 10°.

The results obtained in these experiments show a very close parallelism between the coagulation process in which adsorption takes place and the subsequent change of the coagulate in which there is a reversal of the adsorption. Both are auto-catalytic, and are quite similarly influenced by change of temperature, by change in concentration of the substance adsorbed, and by the addition of protective colloids.

In a final section of the paper, a number of phenomena are referred to which find a satisfactory explanation on the basis of the facts which have been brought to light by the investigation of the velocity of coagulation and reversed adsorption. H. M. D.

Tate's Law. J. Livingston R. Morgan (*Zeitsch. physikal. Chem.*, 1915, **89**, 385—410).—Polemical against Lohnstein (A., 1909, ii, 25; 1913, ii, 926). From an examination of the data for 100 different liquids, the surface tension of which has been measured both by the method of capillary rise and by the determination of the weight of falling drops, it is found that in 69 cases the values obtained agree to within a few tenths of 1%. The remaining 31 liquids are such as cannot easily be obtained in a state of perfect purity, and for this reason the comparison of the two sets of values may show differences which are not characteristic of the pure substances. On the basis of this comparison, a new criterion for a normal liquid is suggested. According to this, a liquid is non-associated when the substitution of the observed values of the surface tension γ and the density d at the temperature t in the equation $\gamma(M/d)^{\frac{2}{3}}=2{\cdot}115(t_c-t-6)$ gives values for t_c which are independent of the temperature at which the measurements are made. This equation has been found to give very satisfactory results in the case of 56 liquids to which it has been applied.

H. M. D.

The Transition from Orderly to Turbulent Flow in Capillary Tubes. II. and III. Walther Sorkau (*Physikal. Zeitsch.*, 1915, **16**, 97—101, 101—102. Compare A., 1914, ii, 539).—II. The change from orderly to turbulent flow in the passage of a liquid through a capillary tube may be determined by the intersection of the curves which correspond with these two modes of flow. The data for acetone, ethyl acetate, water, and chloroform at different temperatures show that, for each liquid, the critical pressure p and the critical time of flow are connected by the equation $\sqrt{p}\,.\,t=c$, where c is a constant equal to 59·0 for acetone, 61·3 for ethyl acetate, 63·9 for water, and 77·5 for chloroform. These constants vary as the square root of the density of the liquids, and the relation between p and t may therefore be expressed by the general equation $\sqrt{p}\,.\,t=64{\cdot}05\sqrt{d}$.

It follows from this that the tendency towards the change from the Poiseuille to the turbulent mode of flow increases with the density and diminishes with the viscosity of the liquid. The

results obtained with benzyl alcohol and mercury are in agreement with this relation. Benzyl alcohol has about the same density as water, but is five times as viscous, and the turbulent condition of flow is only attained at much higher pressures than are required in the case of water. On the other hand, mercury has about the same viscosity as water, but a much greater density, and the turbulent condition of flow is attained at comparatively low pressures.

III. For the same capillary tube, it is shown that the critical velocity of flow U is related to the constant k in the formula for the Poiseuille condition of flow, $pt=k$, by the equation $UD/k=$constant, in which D is the density of the liquid. If the critical velocity only depends on the diameter of the capillary, this equation is of the same form as the relation pointed out by Osborne-Reynolds. H. M. D.

Diffusion and Absorption of Hydrogen in Quartz Glass. HERMANN WÜSTNER (*Ann. Physik*, 1915, [iv], **46**, 1095—1129).—The rate of diffusion of hydrogen through fused quartz has been measured in a series of experiments at 300° to 1000°, and at a pressure of 800 to 900 atmospheres. The relationship between the coefficient of diffusion and the temperature is exponential in character. The coefficient at 1000° is of the same order of magnitude as the coefficient of diffusion through water at the ordinary temperature. From experiments made with a different form of apparatus at a pressure of 3 atmospheres, it is found that the rate of diffusion at 1000° is approximately proportional to the pressure. In connexion with the diffusion experiments, attention is called to the fact that comparable results can only be obtained when fresh quartz is used for each measurement.

The absorption of hydrogen has also been examined by experiments with fibrous quartz (diameter of fibres 0·01 cm.). The absorption-coefficient increases from about 0·0055 at 300° to about 0·011 at 900°. At 1000° it seems to be somewhat smaller than at 900°. H. M. D.

Method for the Calculation of the Hydration of the Ions at Infinite Dilution, and the Ideal Diffusion Coefficient as Applied to the Hydrodiffusion of Electrolytes. GEORGE MCPHAIL SMITH (*J. Amer. Chem. Soc.*, 1915, **37**, 722—733).—The ideal diffusion coefficient, I, obtained by dividing D, the diffusion coefficient, by M, the molecular weight of the particular compound, has been applied to the diffusion of dissolved substances in water, and a new fundamental law of diffusion, $K=IM^n$ or $K=DM^{n-1}$, has been obtained, by means of which a study has been made of certain dilute, liquid amalgams (A., 1914, ii, 543; 1915, ii, 89).

It is now shown that an analogous method can be used in the investigation of the hydration of the ions, the ionic mobilities in this case being treated in the same manner as were the diffusion coefficients of the metals in the study of the constitution of dilute, liquid amalgams. The values $l/$M, where l is the ionic mobility, are proportional to the ideal diffusion coefficients, D/M, of the

ions in question. From a consideration of existing data, it is shown that the law $lM^{n-1}=K$ is valid.

When the hydration of the ions is taken into consideration, the diffusion of highly dissociated electrolytes is found to be essentially no more complicated than that of the non-electrolytes, and in this case, also, the values of K can be calculated by means of the law $K=DM^{n-1}$. A formula has been deduced for the calculation of the diffusion coefficients of hydrated uni-univalent electrolytes at 18° and in 0·01N-concentration. E. G.

Counter Diffusion in Aqueous Solution. GEORGE STANLEY WALPOLE (*Biochem. J.*, 1915, **9**, 132—137. Compare A., 1914, ii, 629).—The author has carried out a number of diffusion experiments in the same way as Osborne and Jackson (*loc. cit.*), but has made more complete analyses of the mixtures after diffusion. Two solutions of potassium chloride of the same concentration and volume were separated from one another by a tap; the lower of the two solutions also contained a measured concentration of an added substance. In the present experiments, the added substances were nitric acid (0·790N), barium hydroxide (0·25N), ammonium hydroxide (0·773N), and ammonium sulphate (3N). After diffusion had taken place across the small cross-section offered by the bore of the tap, the tap was closed, and the solutions analysed. In the case of nitric acid, it is shown that the concentration of potassium ion has increased in the bottom layer, whilst that of chlorine ion has decreased, hydrogen and nitrate ions having both decreased in the lower layer, but the hydrogen ion to a greater extent than the nitrate ion. Similar results are observed in the other cases, the diffusion of the ions with greater migration velocities being greater than those with smaller migration velocities. Counter diffusion is defined as the differential migration of ions of a second electrolyte introduced into a system, whereby all potential gradients are neutralised. Counter diffusion becomes of particular interest in its relationship to the theory of liquid boundary potential differences. J. F. S.

Spontaneous Crystallising Power. PAUL OTHMER (*Zeitsch. anorg. Chem.*, 1915, **91**, 209—247).—The number of crystalline nuclei which make their appearance in piperonaldehyde, undercooled to a definite extent, varies from experiment to experiment, strictly in accordance with the law of probability, all conditions being kept uniform. There is no indication of a discontinuity at any temperature which would correspond with Ostwald's metastable limit. This is confirmed by experiments with phenol and several other organic substances.

The number of nuclei in piperonaldehyde at a given degree of undercooling depends on the temperature to which the substance has been heated previously above its melting point, being smaller the greater the superheating. This suggests that anisotropic molecules are present even in the liquid phase, but that their number diminishes rapidly with increasing temperature. The change is

not reversible, that is, anisotropic molecules are not formed from isotropic above the melting point. On prolonged heating, a limiting value for the number of nuclei is reached. Similar observations have been made with 4-bromo-1 : 3-dinitrobenzene, betol, and palmitic acid.

The fatty acids and their esters, which show an abnormally large change of entropy on fusion, behave abnormally in respect to the number of nuclei, which increases rapidly with increasing undercooling, and diminishes with the extent of the previous superheating. The change of anisotropic molecules into isotropic only proceeds slowly.

Trimyristin, tristearin, and other triglycerides which form unstable modifications allow of the determination of the crystallisation curves for both forms. As the curves cut one another, it is possible by undercooling to a certain temperature to observe the simultaneous appearance of both kinds of nuclei. The following melting points are found: trimyristin, stable 55°, unstable 41·8° and 32·1°; tristearin, stable 70·8°, unstable 64·5° and 54·5°; trilaurin, stable 44·3°, unstable 34·0°; tripalmitin, stable only, 62°.

The influence of metals on the number of nuclei is attributed to solution of some unknown substance, and not to contact action. Thus iron, platinum, and palladium increase the number of nuclei in piperonaldehyde, whilst silver, copper, and nickel are almost without influence. The order is different with betol. The nuclei appear uniformly through the liquid, and not at the surface of the metal. After each successive fusion, the influence of the wire diminishes, whilst the influence often persists after removal of the metal wire. C. H. D.

Velocity of Crystallisation from Aqueous Solutions. N. P. CAMPBELL (T., 1915, **107**, 475—480).—An investigation of the relationship between the velocity of crystallisation and the area of the surface receiving the crystalline deposit. The method consisted in suspending two weighed crystals of potassium alum in a slightly supersaturated solution of the same substance, so arranged that the temperature was slowly falling during about fourteen hours, at the end of which time the crystals were removed and weighed. The results showed that the rate of growth on similar crystal faces was proportional to the exposed area of the faces, or, in other words, large and small crystals received deposits of equal thickness in the same time. Large crystals do not therefore grow at the expense of small ones, as is often stated, and the result also is not in accordance with the conclusion of Richards and Archibald (A., 1901, ii, 546) that the mass deposited is proportional to the time.

It was found, incidentally, that Portland cement added to alum solution caused the complete suppression of the octahedral faces, and the alum crystals obtained were perfect cubes. G. F. M.

The Atomistics of Chemical Reactions in Anisotropic Media. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1915, **91**, 263—276).—Two kinds

of molecules, when present in an isotropic mass or glass, are quite irregularly distributed, whilst their distribution in a crystalline solid solution is regular. It is therefore to be expected that chemical reactions should proceed more readily to completion in a crystal than in a glass. For example, if a crystal containing an equal number of *A* and *B* molecules changes at a definite temperature into a new compound, *AB*, the molecules are most favourably situated; the reaction, therefore, proceeds rapidly, and the new crystal has a definite orientation with respect to the old. If destruction of the solid solution takes place, the new crystallites grow in a definite orientation with respect to the original crystal, but may pass the limits of the original grains in a conglomerate. A section of such a transformed conglomerate may therefore show a double system of polygonal boundaries.

The presence of an excess of one component in an anisotropic mass may completely arrest the reaction. The limits of this effect are discussed mathematically, and tested by application to crystalline solid solutions of silver bromide and iodide. These are rendered homogeneous by prolonged heating at 300°, and are then transferred to a bath at 150° and slowly cooled. Thin layers between glass are used. The appearance of a turbidity is the most sensitive indication of a transformation. It is found that mixtures rich in silver bromide no longer show the transformation, and very prolonged heating at 280° (thirteen days) has the effect of displacing this limit towards mixtures richer in iodide.

C. H. D.

[Theory of Allotropy.] H. R. Kruyt (*Zeitsch. physikal. Chem.*, 1915, **89**, 464—466).—Polemical against Smits (compare A., 1910, ii, 195, 400; 1913, ii, 393, 933). H. M. D.

The Quantitative Determination of the Coagulating Power [of Electrolytes] towards Hydrosols. Otto Hauser and A. Lewite (*Kolloid Zeitsch.*, 1915, **16**, 33—36).—The method used by Freundlich (compare A., 1912, ii, 1044) for comparing the coagulating powers of electrolytes is subjected to criticism, and a new method is suggested. In the application of this method, experiments have been made with the hydrosol form of tantalic acid, which is characterised on the one hand by great stability in pure aqueous solution, and on the other is extremely sensitive to electrolytes.

A definite volume of the hydrosol is titrated with a solution of an electrolyte of known concentration, and the volume required for coagulation is determined. The end-point is, in general, quite sharp. The titration process is repeated with solutions of gradually diminishing concentration, and in this way the influence of the concentration of the electrolyte on the coagulation is obtained. The product of the volume of the solution and its concentration increases with falling concentration, and the results indicate that at a certain concentration the addition of an unlimited quantity of the electrolyte solution will fail to coagulate the hydrosol.

It is shown that the data may be used in the derivation of comparative values for the coagulating power of various electrolytes. Solutions of equal coagulating power were found to contain 8·00 millimols. of sulphuric acid per litre, 2·45 millimols. of barium chloride, and 1·46 millimols. of cerium nitrate.

H. M. D.

[**The Quantitative Determination of the Coagulating Power of Electrolytes towards Hydrosols.**] H. FREUNDLICH (*Kolloid. Zeitsch.*, 1915. **16**, 36—39).—The titration method used by Hauser and Lewite (preceding abstract) is subjected to criticism. On account of the large differences in volume in the experiments with differently concentrated solutions of the electrolytes, it is difficult to interpret the experimental observations. It would seem that the coagulation is not essentially influenced by the concentration of the added electrolyte solution, but that coagulation takes place when the total quantity of the electrolyte suffices to reduce the electrical charge of the colloid particles to a value at which the coagulation takes place rapidly.

The determination of the velocity of coagulation is considered to afford the best means of comparing the coagulating powers of electrolytes. From experiments with aluminium hydroxide sol at 25°, it has been found that solutions containing 100 millimols. of ammonium chloride, 14 of potassium benzoate, and 0·09 of potassium ferrocyanide per litre show the same coagulation velocity. Differences of the same order are found when the coagulating powers of these electrolytes are determined by the method described by the author in previous papers (compare A., 1912, ii, 1044), and this agreement between the two series of data affords some justification for the application of this method in preference to the method of Hauser and Lewite. H. M. D.

Connexion Between the Limit Value and the Concentration of Arsenic Trisulphide Sols. H. R. KRUYT and JAC. VAN DER SPEK (*Proc. K. Akad. Wetensch. Amsterdam.* 1915, **17**, 1158—1163).—Theoretical considerations indicate that the limit value should be independent of the concentration of the sol for univalent cations, and should increase with the concentration for bi- and ter-valent cations. Measurements were made with arsenious sulphide sols of different concentrations, and the limit value for potassium chloride proved to be sensibly constant, whilst it increased with the concentration of the sol, using barium chloride, and still further increased for the aluminium ion. In order to exclude completely the complication of the difference in dispersity degree, the experiments were repeated, using a series of sols prepared by diluting with water an original concentrated sol. Similar results were obtained, except that the limit value for the K ion exhibited a slight, at present unexplained, depression with increasing sulphide concentration. G. F. M.

Action of Nuclei in Gels. R. ED. LIESEGANG (*Kolloid Zeitsch.*, 1915, **16**, 76—79).—A discussion of the mode of action of nuclei

in the transformation of unstable systems, with special reference to gel systems. H. M. D.

Hydrous Chromic Oxide. C. F. NAGEL, jun. (*J. Physical Chem.*, 1915, **19**, 331—337).—From experiments in which an excess of potassium hydroxide was added to solutions containing ferric chloride and chromic sulphate in variable proportions, it has been found that the iron is not precipitated in presence of excess of the chromic salt, and that the chromium is completely precipitated with the iron when the ferric salt is present in considerable excess. It is supposed that these effects are due to mutual adsorption. In a similar way, the hydroxides of manganese, cobalt, nickel, copper, and magnesium are absorbed by colloidal chromic hydroxide, whilst this is also adsorbed and removed from solution by the above hydroxides when these are present in relatively large quantities.

Ferric hydroxide is not precipitated in presence of glycerol, and this is supposed to be due to the formation of a colloidal solution. In presence of copper, chromium is not precipitated by ammonia, and it is suggested that this may be due to the presence of colloidal cupric hydroxide, which adsorbs the chromic hydroxide. It is possible that the hydroxides of the heavy metals in alkaline solutions of sucrose are present in the colloidal form.

Chromic oxide jellies may be obtained by the addition of potassium hydroxide to solutions of chromic sulphate, but the alkali must be added quickly, and not in large excess.

H. M. D.

Osmotic Compressibility of Emulsions and the Influence of the Proximity of Boundary Walls on the Activity of the Brownian Movement. R. COSTANTIN (*Ann. Physique*, 1915, [ix], **3**, 101—120).—In part, a further account of the work which has been described in previous papers (compare A., 1914, ii, 438, 445). By counting the number of colloidal particles present in a small element of volume of gamboge emulsions varying in concentration from 0·28 to 7·6%, it is found that the relation between the number of particles in unit volume and the concentration of the emulsion is in agreement with that represented by an equation of the van der Waals' type. The observed facts point to the existence of a negative internal pressure, which is in all probability due to the repulsive forces acting between the electrically charged particles.

The influence of boundary walls on the Brownian motion of the colloidal particles has been examined, and it is shown that Stokes' formula is not applicable to the movement in these circumstances. On account of this disturbing effect, a correction must be applied to the value of the Avogadro number, which is derived from Einstein's formula. H. M. D.

Theory of Emulsification. VI. WILDER D. BANCROFT (*J. Physical Chem.*, 1915, **19**, 275—309. Compare A., 1913, ii, 680).—An emulsifying agent is a substance which tends to accumulate in

the surface separating two liquids. This phenomenon is discussed, mainly on the basis of the work of earlier observers (Winkelblech, A., 1907, ii, 17; Hofmann, A., 1913, ii, 559).

When small particles of a solid are shaken up with water and a non-miscible, organic liquid, they tend to pass into the water layer if they adsorb water much more readily than the organic liquid, and into the organic liquid if this is adsorbed much more readily than water. If the two liquids are adsorbed simultaneously, the solid particles will accumulate in the liquid–liquid interface. The simultaneous adsorption of both liquids probably produces a new homogeneous liquid phase at the surface of the particles.

A substance which passes into the liquid–liquid surface of separation (dineric interface) is termed interfacial in regard to these two liquids. Such a substance, in the form of a suspension in a given liquid, can be removed by the addition of a second liquid if this is chosen so that the substance tends to accumulate in the liquid–liquid interface. When the interfacial substance forms a coherent and stable film, a stable emulsion is the result. The method recommended by Winkelblech (*loc. cit.*) for the removal of colloid substances from solution affords a means of detecting interfacial substances. It may be used as a method for the detection of peptonised substances in presence of substances which are in true solution.

Reference is made to Tomlinson's experiments (*Phil. Trans.*, 1871, **161**, 51) on the action of oils on supersaturated solutions. According to these, supersaturated solutions of sodium sulphate begin to crystallise on the addition of oils if the oil spreads on the surface of the solution, but are not affected if the oil does not spread. If the ions are strongly adsorbed at the oil–water surface, it is possible that the crystallisation may be due to the oil, but the actual experiments are not sufficient to show that this is the cause.

H. M. D.

Hydrogenisation Equilibria. M. Padoa and B. Foresti (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 84—91).—The authors have sought to apply Nernst's theory for the calculation of equilibrium constants from thermal data to the study of the following two equilibria: (1) $3CHMe_2{\cdot}OH + C_6H_6 = C_6H_{12} + 3COMe_2$; (2) $CHMe_2{\cdot}OH + COEt_2 = COMe_2 + CHEt_2{\cdot}OH$.

In the former case, Nernst's theory leads to the value $K = 0{\cdot}394$, whilst by keeping the substances in the presence of nickel at 185° for 67—140 hours, and estimating the quantities of the different substances then present, the authors calculate the value $K = 0{\cdot}23$. In the second equilibrium, copper was employed as the catalyst at a temperature of 155—160°, the duration of one experiment being 120 hours, and of another 180 hours. From these experiments, the values 3·45 and 2·67 were calculated respectively, whilst from Nernst's theorem $K = 2{\cdot}15$ or $K = 4$, according to the values adopted for the thermal data.

R. V. S.

Influence of Salts on the Equilibrium in the System Water-Acetone. J. W. J. JACOBS (*Chem. Weekblad*, 1915, **12**, 312—320).—Eight ternary systems have been examined, the metallic salts being: (1) NaCl; (2) NH_4Cl; (3) $NaNO_3$; (4) KNO_3; (5) $(NH_4)_2SO_4$; (6) Li_2SO_4; (7) Na_2SO_4; (8) $CaCl_2$. Three quaternary systems have also been investigated, the metallic salts in contact with the water and acetone being: (9) NaCl and $CuCl_2$; (10) NH_4Cl and $BaCl_2$; (11) $(NH_4)_2SO_4$ and Li_2SO_4. For the first system, the critical temperature (T_k) below which further addition of sodium chloride does not cause separation of the water and acetone is $-3{\cdot}8°$. The composition of the critical solution (L_k) is acetone (A) 54%, sodium chloride (S) 6%, and water (W) 40%. For the other systems, the corresponding values are as follows: (2) T_k 18·5°, A 57%, S 6%, W 37%; (3) T_k 41·3°; (4) T_k 61·2°; (5) T_k below $-20°$; (6) T_k not much below $-20°$; (7) T_k 29·6°, A 12%, S 13%, W 75%; (8) constants not determined. For the other three quaternary systems, the observed data do not admit of such ready summary. A. J. W.

Application of the Idea of Expansibility Tension to the Theoretical Study of Hydrates. L. GAY (*J. Chim. Phys.*, 1915, **13**, 33—51).—A theoretical paper in which the author discusses the stability of hydrates and the conditions which determine the equilibrium between two hydrates containing different amounts of water, and between solid hydrates and their saturated solutions. H. M. D.

Univariant Systems Formed by Hydrolysable Salts of Limited Solubility and a Method of Physico-chemical Analysis. E. I. SCHPITALSKI (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 641—681. Compare A., 1914, ii, 634).—In view of the inadequacy of the known physico-chemical methods of analysis to deal with more or less complex systems of ions and molecules, the author has developed an analytical method, based on the following considerations.

Every hydrolysable salt is capable of existing in the solid state in equilibrium with its solution only between two definite concentration limits of the undissociated molecules of the corresponding acid. With definite concentrations of the undissociated acid molecules, H_2X, correspond definite values of the concentration product of the ions into which it dissociates. These products,

$$[H^{\cdot}]^2[X^{''}]=B_1 \text{ and } [H^{\cdot}][HX^{'}]=B_2,$$

termed stability products, determine the interval of stability of the salt. The absolute magnitudes of the stability products for a given salt depend on the temperature alone, and not on the presence of any foreign substance in the solution. In the case of a solution saturated at the same time by two salts capable of interconversion, all the non-dissociated molecules, in the form of which the acid and salts are capable of existing, occur in perfectly definite concentrations depending solely on the temperature. Since the general composition of the solution is not changed by the influence

of a foreign acid, such solution will contain undissociated molecules in constant concentration, and the ionic concentrations will give one and the same solubility product and one and the same stability product. Consequently, comparison of the estimations of the total acid and total base in equilibrated solutions with different concentrations of the foreign acid renders possible the calculation, first, of the separate concentrations of the various ions of the acid in each solution, and, secondly, of the equilibrium constant.

These principles are applied to several different cases, of which the conditions of dissociation of a monobasic acid, HX, and its salt, RX, may be given by way of example. In general, the solution will contain the following ions and molecules: $H^{\cdot}$, X', HX, $R^{\cdot}$, and RX, and for a saturated solution the composition will be expressed by the equations $[H^{\cdot}][X']=L$, $[R^{\cdot}][X']/[RX]=K$, $[H^{\cdot}]+[R^{\cdot}]=[X']$, $M=[X']+[HX]+[RX]$, and $R=[R^{\cdot}]+[RX]$, where M denotes the total concentration of the given acid and R that of the base. These five equations contain seven unknowns. When R is altered to R_1, the concentration [HX] and the constants L and R remain as before, but the other concentrations change to $[H^{\cdot}]_1$, $[X']_1$, $[R^{\cdot}]_1$, and $[RX]_1$, so that the ten equations contain eleven unknown quantities. A further change of R adds five equations and four unknowns, making a total of fifteen equations and fifteen unknowns. The solution of these is, however, complicated by the variation of the denominator, [RX], of the second equation, three cubic equations with three unknowns resulting. The application of this method to a univariant system with two co-existing solid phases is more simple. Thus, for solutions saturated with respect to HX and RX, and differing as regards the value of a small known concentration of a strong acid, such as nitric acid, the following equations hold: $[H^{\cdot}][X']=L$, $[R^{\cdot}][X']=L_1$, $[H^{\cdot}]+[R^{\cdot}]=[X']+n$, $M=[X']+[HX]+[RX]$, and $R=[R^{\cdot}]+[RX]$, n being the ionic concentration of the nitric acid. The value of [RX] is now constant, and two different values of n are sufficient to give ten equations with ten unknown quantities. The solution thus presents no difficulty, and when L and L_1 and the values of [HX] and [RX] are known, the equilibrium constants are given by the equations $[H^{\cdot}][X']/[HX]=K$ and $[R^{\cdot}][X']/[RX]=K$.

These considerations are further applied to: (1) the dissociation of a dibasic acid, H_2X, and its salts, R_2X and RHX; (2) the dissociation of a tribasic acid, such as orthophosphoric acid, H_3PO_4, and its salts, RH_2PO_4, R_2HPO_4, and R_3PO_4; (3) the calculation of the equilibrium relations of chromic and dichromic acids from Sherrill's results (A., 1908, ii, 92). The equilibrium constant, $K=[Cr_2O_7'']/[HCrO_4']^2$, is thus found to have the value 52·1, whereas Sherrill's calculations gave the number 75, and Beck and Stegmüller (A., 1910, ii, 1067) found 0·4.

The above method may naturally be employed in the investigation of the transformations of complex bases, as well as of complex acids. With reference to the limitations of the method, it is necessary, first, that the substance investigated should form mutually transformable compounds with comparatively low solubilities. so

that concentrated solutions may be avoided, and, secondly, that these solubilities should be sufficient for the requirements of chemical analysis. Another restriction rests on the possibility of excessively complex transformations of the compound to be investigated, increase in the number of unknowns, and especially of variable unknowns requiring the combination in one series of equations of an increased number of experimental results, besides rendering the calculated results more susceptible to experimental errors. Where possible, it is advantageous to employ the method in conjunction with, for instance, electrometric measurements of the concentration of hydrogen or metallic ions, but such measurements must be carried out with the same saturated, equilibrated solutions. Another limitation is furnished by the necessity of preliminary knowledge of the conditions of dissociation of the auxiliary compound, with the aid of which the ionic composition of the solution is varied without change of the concentrations of the non-dissociated molecules; this limitation, however, loses much of its force, since in most cases the concentration of the auxiliary compound should vary only within the limits 0—0·1N, the concentrations of the other electrolytes being also comparatively small.

T. H. P.

Physico-chemical Kinetics. R. MARCELIN (*Ann. Physique*, 1915, [ix], **3**, 120—184).—A theoretical paper, in which the views brought forward in a previous paper (compare A., 1914, ii, 115) are discussed in greater detail. The method of evaluating the critical energy necessary to transform a molecule from the zero state into the active state (compare A., 1914, ii, 186) is also examined more closely.

H. M. D.

Physico-chemical Kinetics. R. MARCELIN (*Ann. Physique*, 1915, [ix], **3**, 185—231. Compare preceding abstract).—By application of the kinetic theory to the molecular exchange at the surface of contact of a liquid and its vapour, it is shown that the maximum rate of evaporation, as measured by the rate of change in the level of the surface of the liquid, is given by the equation

$$V = 4{\cdot}38 \times 10^{-5}(P - p)\sqrt{M/T}/d,$$

in which P is the pressure of the saturated vapour at temperature T, p the actual pressure of the vapour, M the molecular weight of the liquid, and d its density. If all the molecules of vapour which impinge on the surface of the liquid are not absorbed, the velocity will be smaller, and if v is the observed velocity of evaporation, the ratio v/V represents the fraction of the vapour molecules which are absorbed on reaching the surface of the liquid.

An attempt has been made to determine the value of this fraction by measurements of the rate of evaporation of nitrobenzene and of the rate of sublimation of naphthalene and iodine in a vacuum. The substances were contained in capillary tubes of 0·1 to 0·3 mm. internal diameter, which were immersed in a thermostat, and the rate of fall of the surface of the liquid or solid was determined by observations at different temperatures. The ratio

of the number of molecules of vapour which come into contact with the surface of the liquid or solid to the number of molecules which are absorbed at this surface is given by $N = V/v$. The value of N for nitrobenzene falls from 15 at 40° to 4 at 65°, for naphthalene from 28 at 40° to 7·4 at 70°, and for iodine from 18 at 40° to 4·8 at 70°. In all cases, the ratio diminishes with rising temperature, indicating that the molecular exchange at the contact surface is a process which shows considerable dependence on the temperature.

From a further series of experiments in which the rate of evaporation of liquids, superheated to the extent of a few millimetres of mercury, was examined, it has been found that the velocity of vaporisation may be expressed by the equation $v = K(T_B - T_P)/dl$, in which K is a constant, T_B the temperature of the bath in which the capillary tube is immersed, T_P the temperature of equilibrium corresponding with the pressure P in the apparatus, d the density of the liquid, l its latent heat, and r is the radius of the capillary tube. From these results, the author draws the conclusion that the temperature of the liquid surface is not that of the surrounding bath, but is approximately equal to the equilibrium temperature which corresponds with the pressure P. It is also probable that the observed rate of vaporisation is determined by the rate at which heat is supplied to the liquid, and that the true velocity of vaporisation is very large in comparison with the observed value.

H. M. D.

The Temperature-coefficient of Photochemical Reactions. Daniel Berthelot (*Compt. rend.*, 1915, **160**, 440—443).—The temperature-coefficient, K_{t+10}/K_t, for ordinary chemical reactions is between 2 and 3. For photochemical reactions it is, however, very near to unity. The velocities of decomposition of lævulose by ultraviolet rays at 70° and 40° respectively bear the ratio 1·035 : 1. The velocities of reduction of ferric chloride by oxalic acid in aqueous solution in daylight at 61° and 21° respectively bear the ratio 1·01 : 1. In photochemical reactions, variation of the wavelength controls the rate of action, as in ordinary chemical reactions variation in temperature does. W. G.

Kinetics of Photochemical Reactions. Daniel Berthelot (*Compt. rend.*, 1915, **160**, 519—522).—A mathematical paper in which the author shows that the kinetic considerations which apply to ordinary reactions apply equally to photochemical reactions, providing that electrons are substituted for molecules. These reactions are almost all of the first order, and present two notable differences from thermal reactions. First, they are only of the first order when they occur in dilute solutions in thin layers (compare A., 1913, ii, 267). Secondly, under the influence of light, the particles assume much greater velocities than under the influence of heat, and photochemical reactions have a thermal coefficient very near to unity (compare preceding abstract). W. G.

Halogen Oxygen Compounds. IX. Kinetics of the Bromate-Bromide Reaction. ANTON SKRABAL and SIEGFRIED R. WEBERITSCH (*Monatsh.*, 1915, **36**, 211—235. Compare A., 1907, ii, 448; 1909, ii, 224; 1911, ii, 382; 1912, ii, 33, 340; 1914, ii, 623).—The kinetics of the reaction $BrO_3' + 5Br' + 6H^{\cdot} = 3Br_2 + 3H_2O$ have been studied by the methods of Clark (A., 1907, ii, 77), Miller and others. It is shown that the velocity of the reaction is proportional to the product of the concentrations of the bromate and bromide ions multiplied by the square of the concentration of the hydrogen ion. This is a confirmation of the work of Judson and Walker (T., 1898, **73**, 410), $d(BrO_3')/dt = k[BrO_3']/[Br'][H^{\cdot}]^2$. The addition of a neutral salt to the reaction mixture has little or no influence on the velocity of reaction. The velocity constant at 25° is shown to have the value 200. From measurements carried out at 18° and 25·3°, the temperature-coefficient is shown to be 2, whilst from experiments at 32·6° and 25·3° the value 1·9 is obtained. The addition of chlorine ions to the reaction mixture increases the velocity of the reaction. J. F. S.

Colloidal and Catalytic Properties of Mineral Waters of Roumania. Complications Due to the Presence of Salts. EMILE GIURGEA (*Bull. Acad. Sci. Roumanie*, 1914, **2**, 192—201).—The colloidal and catalytic properties of a number of spring waters containing sulphur compounds and carbonates are expressed by a number, termed the "catalytic coefficient." This is determined by measuring the quantity of hydrogen peroxide destroyed by a measured quantity of the water at 37° in one hour. The electro-conductivity of the same water is also given, and it is shown that the colloidal properties, as measured by the "catalytic coefficient," are not directly related to the conductivity. J. F. S.

Variation of Catalytic Power of Saline and Colloidal Solutions with Concentration. EMILE GIURGEA (*Bull. Acad. Sci. Roumanie*, 1914, **2**, 216—219).—The catalytic action of very dilute solutions of sodium carbonate, ammonium chloride, potassium chloride, sodium chloride, sodium hydroxide, potassium hydroxide, colloidal mercury, and some colloidal medicinal preparations have been determined in several concentrations by the rate of decomposition of hydrogen peroxide. In the case of sodium carbonate and ammonium chloride, it is shown that a slight increase in concentration produces a large increase in catalytic power, which, with a further increase in concentration, rapidly reaches a maximum. The increase in concentration of sodium chloride and potassium chloride is less pronounced, and a maximum has not been reached by $N/10$-solutions. With colloidal metals, the concentration curves show that the catalytic power increases slowly with dilute solutions on increasing the concentration, and then much more rapidly, with further increase in concentration, than in the case of salts. With alkali hydroxide, the catalytic power increases rapidly to a maximum, which is reached with approximately $N/500$-solutions, and then falls off rapidly, and is very small with $N/10$-sodium hydroxide. J. F. S.

Influence of Alkalinity in the Determination of the Catalytic Coefficient. EMILE GIURGEA (*Bull. Acad. Sci. Roumanie*, 1914, **2**, 220—224).—The alkalinity and catalytic power of a number of salts in $N/10$-solution have been determined. The alkalinity is determined by measuring the volume of $N/10$-sulphuric acid required to change the tint of a drop of methyl-orange added to the solution, and the catalytic power by the action of the solution on hydrogen peroxide. It is shown that there is no direct relationship between the two quantities. The catalytic power of colloidal solutions of sulphur is measured by the same method, and it is shown that this quantity increases with the concentration. The properties of colloidal sulphur solutions are discussed in connexion with their medicinal uses, and in their connexion with sulphur mineral waters. J. F. S.

Oxidation of Alcohols in Presence of Ferrous Oxide or Ferrous Salts. A. G. DOROSCHEVSKI and A. J. BARDT (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 754—785).—The authors have investigated the oxidation of a number of alcohols by charcoal and by various oxidising agents in presence of ferrous oxide or a ferrous salt.

The varying oxidising properties of charcoal are related to the varying contents of adsorbed oxygen, and when the latter is completely absent from the charcoal, and the alcoholic solution contains no dissolved oxygen, formation of aldehyde does not take place. The presence of oxygen is not, however, the only condition necessary for the oxidation of alcohol by charcoal. Just as the ability of charcoal to adsorb colouring matters depends on the presence of certain salts and nitrogen compounds (compare Glassner and Suida, A., 1908, ii, 669), and the catalytic decomposition of alcohols on the presence of silicon compounds (compare Senderens, A., 1908, i, 495; 1908, ii, 166), so the oxidising properties of charcoal are related to the presence of compounds of iron.

Methyl, ethyl, propyl, *n*- and *iso*-butyl, and *iso*amyl alcohols are oxidised by potassium permanganate or hydrogen peroxide in presence of ferrous salts, ferric and manganous salts being without catalytic effect on the oxidation. When ferrous sulphate is present, permanganate oxidises ethyl alcohol, in dilute solution, almost exclusively to the aldehyde, but in presence of ferrous oxalate the oxidation proceeds further, part of the aldehyde being transformed into acetic acid; these oxidations proceed so regularly that the course of the reaction may be investigated quantitatively. Hydrogen peroxide acts still more energetically on ethyl alcohol, which, in presence of ferrous sulphate or oxalate, is oxidised to a mixture of acetaldehyde and acetic acid, the aldehyde predominating with the former, and the acid with the latter, catalyst; these oxidations serve as striking lecture experiments, decolorised magenta being used as indicator.

Ferric salts do not increase the oxidising power of charcoal, but addition of a ferrous salt to a solution of alcohol containing charcoal results in considerable increase in the amount of aldehyde

formed. This was found to be the case with thirteen different forms of charcoal obtained from wood or sugar, or of animal origin.

The oxidising properties of charcoal are, therefore, destroyed by either the removal of the adsorbed oxygen or the oxidation of the ferrous compounds present. The above results afford an explanation of the industrial revivification of charcoal effected by igniting it and allowing it to cool in the air.

The oxidation of alcohol by charcoal is an example of a coupled reaction, the charcoal acting as a catalyst: $2FeO + O \longrightarrow Fe_2O_3$ and $Et{\cdot}OH + O \longrightarrow CH_3{\cdot}CHO + H_2O$. T. H. P.

The Cyclic Evolution of the Chemical Elements. II. F. H. Loring (*Chem. News*, 1915, **111**, 181—182. Compare this vol., ii, 249).—A further discussion of the ideas brought forward in the previous paper. H. M. D.

The Eighth Group of the Periodic System. E. H. Büchner (*Chem. Weekblad*, 1915, **12**, 336—339).—An attempt to rearrange the periodic system so as to eliminate group 8. Iron, nickel, and cobalt are placed, along with manganese, in group 7, and the ruthenium and osmium triads are transposed to the blank spaces in the same group. A. J. W.

Criticism of the Electron Conception of Valence. Roger F. Brunel (*J. Amer. Chem. Soc.*, 1915, **37**, 709—722).—The author criticises the so-called electron conception of valence, and objects to it on the grounds that the chemical evidence advanced in dealing with simple phenomena is not convincing; that its application involves the use of assumptions which are not supported by the evidence of physical experiments; that the electromeric formulæ assigned to compounds are inconsistent with any rule which can be proposed; and that no definite case of electroisomerism has yet been established. E. G.

Coupled Reactions or Reactions of Oxidation and Reduction according to S. V. Dain's Electron Theory. Gregory Dain (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 845—863).—The author expounds the formulation of chemical reactions, principally of oxidation and reduction, developed by S. V. Dain in 1910—1911 from the standpoint of the electron theory, and explains thereby the oxidation of ferrous to ferric salts by means of nitric acid, the reduction of ferric chloride by ammonium sulphide, the oxidation of the nickelous to the nickelic ion, and the reaction of (1) the chromate ion with ethyl alcohol; (2) manganous hydroxide with potassium nitrate; (3) the mercurous and the mercuric ions; and (4) oxalic acid with permanganate.

Oxidation-reduction reactions are regarded as composed of three successive processes or phases. In the first of these, which comprises two sub-processes, electrons are transferred from certain atoms to certain others. This is a conjugated process, scission of electrons from one atom being combined with their union to

another. The second phase consists of the formation of new ions from the atoms of the elements taking part in the first phase and in the general reaction. The atoms which have their valency or significance changed in the first phase, and the ions formed in the second phase, together with the remaining unaltered parts of the compounds taken, then take part in a simple reaction of interchange or combination; this constitutes the third phase. These conjugated processes thus fulfil the conditions of the law of the conservation of matter in its relation to electrons.

These principles are capable of application to all chemical reactions, and may serve to indicate the courses of the reactions. In chemical reactions, the transference of electrons proceeds from the first towards the seventh group of the periodic system. As regards elements of any one group: in groups of elements existing in their compounds with an insufficiency of electrons, the latter pass in the direction of diminished atomic weight in the first sub-groups, and in that of increased atomic weight in the second sub-groups; in groups of elements containing in their compounds excess of electrons, the latter proceed in the direction of diminution of the atomic weight. T. H. P.

Arrangement for Automatically Cutting Off the Gas Supply at Definite Volumes. St. Goldschmidt (*Chem. Zeit.*, 1914, **38**, 1023).—An apparatus for automatically extinguishing the gas flame when evaporation has proceeded to the desired extent. It consists essentially of two tubes joined at the top to form two arms, one of which is immersed in the evaporating liquid to the level to which it is desired evaporation shall proceed, and the other is connected outside to one arm of a U-tube, the other arm of which is provided with a gas in- and out-let and a mercury seal similar to the arrangement in an ordinary thermostat. In operation, both the arms of the apparatus are charged with the evaporating liquid or with water, and the mercury is so adjusted that the gas passage is free. When the liquid surface sinks below the opening of the originally immersed arm, the liquid in this arm flows out, whilst that in the other arm is then free to exert a pressure on the mercury, pushing it up the other side of the U-tube slightly, and thus closing the gas passage. G. F. M.

Comparison of the Relative Drying Powers of Sulphuric Acid, Calcium Chloride, and Aluminium Oxide when Used in Ordinary Scheibler Desiccating Jars. J. W. Marden and Vanna Elliott (*J. Ind. Eng. Chem.*, 1915, **7**, 320—321. Compare Johnson, A., 1912, ii, 847).—For drying substances under reduced pressure, aluminium oxide appears to be somewhat more efficient than either sulphuric acid or calcium chloride, particularly when only small quantities of moisture are present. In the case of a large quantity of moisture, aluminium oxide and 95% sulphuric acid have equal dehydrating properties, whilst calcium chloride is less effective. Aluminium oxide has the advantage that, when it becomes saturated with moisture, it may be heated and used again. W. P. S.

Inorganic Chemistry.

Behaviour of Hydrogen Peroxide towards Salts. P. V. KAZANECKI (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1110—1127).—With carbonates of the alkali metals, hydrogen peroxide forms unstable compounds, such as $Cs_2CO_3,2H_2O_2$, $K_2CO_3,2H_2O_2,\frac{1}{2}H_2O$, $Na_2CO_3,1\frac{1}{2}H_2O_2$, which exhibit the properties of peroxides, and at the ordinary temperature decompose, with evolution of carbon dioxide and formation of the corresponding metal hydrogen carbonate as a result of the perhydrolysis of the carbonates. Magnesium carbonate and hydrogen peroxide in solution give the compound $MgO_2,\frac{1}{5}MgCO_3,H_2O$, perhydrolysis of the basic carbonate being again accompanied by loss of carbon dioxide. All these compounds react with titanic acid or dichromate and sulphuric acid, and yield ozone with concentrated sulphuric acid, and chlorine with concentrated hydrochloric acid; from neutral potassium iodide solution they liberate iodine slowly. Perhydrolysis is also observed when hydrogen peroxide solution acts on zinc carbonate or bismuth nitrate.

The increased solubility of salts in hydrogen peroxide solution has been observed by various investigators. In the case of potassium sulphate, this increase is related linearly to the proportion of hydrogen peroxide, the presence of 72·6 grams of the latter per 100 c.c. raising the solubility of the sulphate from 11·11 grams to 67·22 grams per 100 c.c. of solution. That the peroxide and sulphate interact is shown by cryoscopic and conductivity measurements. T. H. P.

The Air of Bucharest. ST. MINOVICI and E. GROZEA (*Bull. Acad. Sci. Roumanie*, 1914, **2**, 275—286).—The authors have made a large number of determinations of the amounts of dust, carbon dioxide, and ozone present in the air of Bucharest. The analyses of the dust were made from air at a height of 1·5 metres from the pavement. Some thirty analyses were made, and the following mean quantities per cubic metre found: in streets paved with asphalt, 0·0062 gram; in streets paved with stone blocks, 0·0066 gram; and in earth-paved country roads, 0·0534 gram. These results are compared with similar results obtained in Berlin and Dresden. Microscopic examination has also been carried out with dust deposits from the same sources, and it is shown that the country roads give a dust containing a large quantity of angular particles, whereas that from asphalt-paved roads contains a quantity of organic fibres. As a mean of more than a hundred determinations of carbon dioxide, a mean value of 3·02 parts per 10,000 is obtained for the town itself, whilst the value 2·81 per 10,000 is found for the surrounding plain. Qualitative tests for the presence of ozone show that, out of ninety-five tests made between

June and December, 1914, forty-eight gave positive results. Hence, apart from the large quantity of dust, the air of Bucharest compares very favourably with that of other large European towns. J. F. S.

Oxidising Properties of Sulphur Dioxide. J. A. SMYTHE and W. WARDLAW (*Proc. Durham Phil. Soc.*, 1913–14, **5**, 187—201).—A summary of hitherto known reactions in which sulphur dioxide behaves as an oxidising agent is followed by an account of the investigation of the oxidising action of this substance on the lower chlorides of tin, titanium, mercury, and iron. Stannous and titanous chlorides were oxidised in warm, strongly acid solution to stannic and titanic chlorides respectively, the sulphur dioxide being reduced to hydrogen sulphide. In solutions not too strongly acid, the corresponding sulphides were accordingly precipitated, otherwise sulphur was formed in quantities corresponding with the equations:

$$3SO_2 + 12HCl + 6SnCl_2 = 6SnCl_4 + 6H_2O + 3S,$$
$$3SO_2 + 12HCl + 12TiCl_3 = 12TiCl_4 + 6H_2O + 3S.$$

In concentrated hydrochloric acid, mercurous chloride was slowly, but completely, oxidised, with the deposition of sulphur; no hydrogen sulphide was formed.

Ferrous chloride was also oxidised in strong acid solution, but only to the extent of about 7% on the average, and increase in the total concentration of the iron lessened the relative amount of ferric salt. The sulphur dioxide was reduced to sulphur. The reaction is not a balanced one, but appears to be brought to a standstill by direct inhibition by the ferric chloride. When more than 14% of the total iron was in the ferric state, no sulphur was deposited on leading in sulphur dioxide, and no oxidation took place at all. It is suggested that the oxidising action of sulphur dioxide in the above cases, which is only manifested in presence of concentrated hydrochloric acid, may be due directly to the intermediate formation of thionyl chloride. G. F. M.

Theory of the Lead Chamber Process. O. WENTZKI (*Zeitsch. angew. Chem.*, 1914, **27**, 512).—Polemical. The author still maintains that account was not taken in Hempel's experiments (A., 1914, ii, 455, 647) of the dissociation, and consequent change in volume, of the nitrogen peroxide, since the gas-introduction tubes were only maintained at 70°, at which temperature dissociation has certainly commenced, but is far from complete. G. F. M.

Solution of Selenium and Tellurium in Absolute Sulphuric Acid. E. MOLES (*Anal. Fis. Quim.*, 1915, **13**, 134—144).—An investigation of the effect of selenium and tellurium on the freezing point of absolute sulphuric acid. With red, amorphous selenium, the solution contains a polymeric form of the compound SO_3Se; grey, crystalline selenium yields the same substance, but in simple molecules. The conductivity of the sulphuric acid is not affected by the solution of selenium.

Tellurium reacts with the acid, the solution giving abnormal values for the molecular weight, and showing an increase in conductivity. A. J. W.

A Chemically Active Modification of Nitrogen Produced by the Electric Discharge. VI. Hon. R. J. STRUTT (*Proc. Roy. Soc.*, 1915, [*A*], **91**, 303—318. Compare A., 1913, ii, 696).—The controversy as to whether active nitrogen can be obtained from pure nitrogen, or whether a trace of oxygen must be present, is reviewed (compare A., 1914, ii, 724). Further experiments have been made which show that neither of these alternatives is correct. Although perfectly pure nitrogen only yields a small quantity of active nitrogen on the passage of the discharge, the admixture of a small quantity of almost any foreign gas increases enormously the yield of active nitrogen. Argon and helium are exceptions, and have no appreciable influence on the intensity of the after-glow, but positive results were obtained with hydrogen sulphide, water, carbon dioxide, carbon monoxide, acetylene, ethylene, methane, oxygen, mercury, chlorine, and hydrogen. The order of the gases in this series affords a rough measure of the catalytic activity of the admixture, the activity diminishing from left to right. The quantity of foreign gas required to produce the maximum effect is usually of the order of 1 part in 1000 of nitrogen, but experiments with methane, in which this point was specially examined, show that a perceptible effect on the yield of active nitrogen is produced by the addition of 1 part of methane to 30,000 of nitrogen.

A sample of nitrogen which gives very little after-glow can be obtained by prolonged treatment of commercial nitrogen with sodium potassium alloy at 300°. The regulated admission of foreign gases into the current of nitrogen passing into the discharge tube is conveniently effected by means of a capillary tube connected with a reservoir of the gas.

In explanation of the above observations, it is suggested that the foreign gas acts by combining with the free electrons, thus altering the character of the impact with the nitrogen molecules. This view is supported by the fact that gases which contain oxygen, sulphur, chlorine, carbon, and hydrogen have been shown to combine readily with electrons in the discharge (compare Franck, A., 1910, ii, 479, 817; Thomson, A., 1911, ii, 457), whilst argon, helium, and nitrogen have not this faculty. The case of mercury is anomalous, for it promotes the formation of active nitrogen, but does not take a negative charge in the canal rays. The anomalous behaviour is probably connected with the fact that mercury atoms in the canal rays carry much larger positive charges than do other atoms.

Further experiments with active nitrogen show that it combines with metals in the liquid state, but the spectrum of the metal is not developed under these conditions. A dilute solution of indigotin in concentrated sulphuric acid is decolorised by a current of active nitrogen. It has no action on glycerol, but reacts with

carefully purified methane, pentane, and heptane, with the formation of hydrogen cyanide. H. M. D.

Synthetic Production of Ammonia. F. HABER (*Zeitsch. angew. Chem.*, 1914, **27**, 473—477).—A review and summary of already published work on the synthesis of ammonia, particularly of the author's researches on the influence of pressure and temperature on the equilibrium of nitrogen and hydrogen, and on the accelerating influence of catalysts on the velocity of the ammonia formation. The technical development of the synthesis as a method for the commercial production of ammonia is described. G. F. M.

Anhydrous Hydrazine. III. Anhydrous Hydrazine as a Solvent. T. W. B. WELSH and H. J. BRODERSON (*J. Amer. Chem. Soc.*, 1915, **37**, 816—824. Compare this vol., ii, 256).—Determinations have been made of the solubilities of a large number of elements and inorganic salts in anhydrous hydrazine with a view to a subsequent study of chemical reactions in this solvent.

Of the metallic elements tested, the alkali metals only were appreciably dissolved; the solubility increases with increase of atomic weight. Sulphur and iodine are very soluble, and cause rapid decomposition of the hydrazine. The solubility of the metallic haloids seems to increase with the increase of atomic weight of the halogen; in the case of the haloids of the alkali earth metals, crystalline substances separate from the solutions, which are probably hydrazinated salts. The carbonates are either insoluble or very slightly soluble. The oxides are all insoluble. The nitrates are mostly soluble, with the exception of those which react with the solvent. Sulphides and sulphates are but slightly soluble. Ammonium salts, except triammonium phosphate, dissolve with evolution of ammonia. Bismuth chloride dissolves, and reacts with the hydrazine, bismuth being quantitatively precipitated. Cadmium carbonate and sulphide are insoluble, but the haloids are very soluble. Mercury sulphide is insoluble, but the other mercury salts react immediately with the solvent, and mercury is precipitated. Nickel and cobalt salts dissolve, and react with the solvent to form hydrazine additive compounds. In the case of cobalt chloride, a cobalt mirror is gradually formed. Copper and lead salts dissolve with more or less decomposition. Silver salts invariably yield a silver mirror. E. G.

Anhydrous Hydrazine. IV. Chemical Reactions in Anhydrous Hydrazine. T. W. B. WELSH and H. J. BRODERSON (*J. Amer. Chem. Soc.*, 1915, **37**, 825—832).—The work described in this paper was undertaken with the object of studying the hydrazine system of acids, bases, and salts, in which the acid hydrazides, metallic hydrazides, and metallic derivatives of the acid hydrazides are regarded as acids, bases, and salts respectively. An investigation has been made of the following reactions in anhydrous hydrazine solutions.

By the action of hydrazine sulphide on cadmium iodide and zinc chloride, cadmium and zinc sulphides are precipitated; the yellow colour of hydrazine sulphide could serve as an indicator in the titration of cadmium and zinc salts. Sodium hydrazide reacts with zinc chloride with formation of a precipitate, which is probably a zinc hydrazide. Sodium precipitates cadmium, zinc, and iron from solutions of their salts, but magnesium, calcium, and barium are not precipitated. Zinc, copper, tin, and aluminium do not react with a solution of hydrazine sulphate in anhydrous hydrazine. Magnesium and calcium do not dissolve in or react with hydrazine, but lithium dissolves slowly with evolution of gas; on addition of hydrazine sulphate, however, gas is rapidly evolved in all three cases, and the metal becomes coated with a white deposit, probably consisting of the sulphate. Sodium and sodium hydrazide react with hydrazine chloride with formation of sodium chloride in each case.

These results show that reactions take place in anhydrous hydrazine similar to those which occur in water, liquid ammonia, and certain other dissociating solvents. E. G.

The Temperature-coefficient of the Formation of Nitrosyl Chloride from Nitric Oxide and Chlorine. MAX TRAUTZ (*Zeitsch. anorg. Chem.*, 1914, **88**, 285—320).—The reaction $2NO + Cl_2 = 2NOCl$ has been studied by means of an apparatus designed for accurate work. The very numerous measurements show that the equilibrium constant increases steadily up to about 130°. The temperature-coefficient is low, about 1·2, diminishing further with increasing temperature, corresponding with the high order and high velocity of the reaction. At higher temperatures, the results are more irregular. Low partial pressures must be employed, as otherwise the contraction is too rapid for measurement, and the high velocity causes uncertainty in the readings. Other compounds, richer in nitric oxide, are also formed to some extent. The experiments have been carried as far as 283°, the divergence from the theoretical form of curve increasing with the temperature.

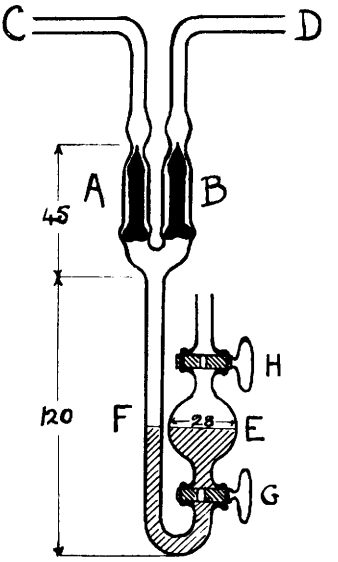
Accurate data regarding the molecular heats of nitric oxide and chlorine are lacking for a theoretical calculation. A suitable choice of data being made from analogy with other gases, the theory is tested. For the first 100° there is complete agreement, but beyond this the observed values become higher than the theoretical. A maximum value for the heat of activation is calculated to be 9958 cal., 9274 cal. being found. The kinetic constant, K, is calculated as 10^{35}, and found to be 2×10^{36}. C. H. D.

A Hydrate of Hydrogen Arsenide. R. DE FORCRAND (*Compt. rend.*, 1915, **160**, 467—470).—The author has prepared a hydrate of hydrogen arsenide by compressing the gas in the presence of a few drops of water, followed by a sudden expansion and a second compression. The solid hydrate can be kept indefinitely between 0° and 28·2°, the dissociation pressures at these two temperatures being, respectively, 0·806 atmos. and 17·5 atmos. Using

Clapeyron's formula, the author calculates the heat of formation of the solid hydrate, from water and the gaseous hydride, to be +17·753 Cal., and from ice and the gaseous hydride +8·238 Cal., which values gave the formula of the hydrate as $AsH_3,6H_2O$. The author has determined for the four hydrides SH_2, SeH_2, PH_3, and AsH_3 the temperatures at which the hydrates have a dissociation pressure of 760 mm., and finds that the difference between these temperatures for hydrogen sulphide and hydrogen phosphide is practically the same as the difference for hydrogen selenide and hydrogen arsenide. The same holds good taking the pairs hydrogen sulphide, hydrogen selenide and hydrogen phosphide, hydrogen arsenide. W. G.

Boron Trichloride. A Greaseless Gas-Valve. ALFRED STOCK and OTTO PRIESS (*Ber.*, 1914, **47**, 3109—3115).—The physical constants of boron trichloride have been determined.

The material was obtained by the action of chlorine on Moissan's boron in a glass tube, the temperature being so regulated that the glass was attacked as little as possible. The crude product, condensed at −80°, was shaken with mercury, and then freed from traces of hydrogen chloride and silicon chloride by fractional distillation in a high vacuum, from a bath at −78°. The early fractions, condensed by liquid air, contained hydrogen chloride, which influenced the vapour pressure at 0° far more than the melting point, whilst the silicon chloride collected in the end fractions. The following constants of a pure fraction were observed; m. p. −107°, b. p. 13°/764 mm. (room temperature −10°), V.D. 58·43, vapour pressure in mm. of mercury at room temperature:



Temp.	−80°	−75°	−70°	−65°	−60°	−55°	−50°	−45°	−40°	−35°
mm.	4	6	9	13	18	26	37	51	67	89
Temp.	−30°	−25°	−20°	−15°	−10°	−5°	0°	5°	10°	12·4°
mm.....	116	151	197	251	314	387	477	579	695	753

The calculated b. p. is 12·5°/760 mm.

Boron trichloride does not attack hot mercury, nor does it combine with chlorine, even at −80°. It reacts energetically with fat, and therefore a valve was designed which had no greased taps to be exposed to the vapour (annexed diagram).

A and *B* are solid glass floats, resting by three feet on the enlargement in the tubes, and ground at the top to fit into the ground constriction. *C* and *D* connect the other pieces of

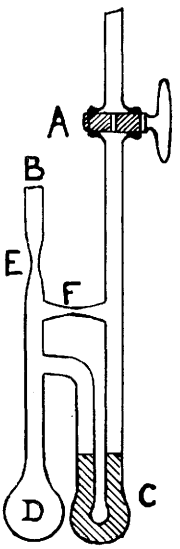
apparatus. The bulb *E* contains clean mercury. When *A* and *B* have fallen, *C* communicates with *D*. By raising the mercury in *F*, the floats are forced into the constrictions, to make, with a thin film of mercury, a gas-tight seal. The floats are made to fall again by evacuating *E* and opening the tap *G*. The numbers refer to millimetres. J. C. W.

Boron Tribromide. Alfred Stock and Ernst Kuss (*Ber.*, 1914, **47**, 3113—3115).—Some physical constants of boron tribromide have been determined.

The compound was obtained by passing bromine vapour over boron at a dull red heat, shaking the product with mercury, and then fractionating under atmospheric pressure with a Hahn column (A., 1910, ii, 183). The following constants are recorded; m. p. −46°, b. p. 90·1°/740 mm., M.W. 252 (cryoscopic method, in benzene), and vapour pressures:

Temp.	−50°	−40°	−30°	−25°	−20°	−15°	−10°	−5°	0°	5°
mm.	0·7	1·5	3	4	5·5	8	10·5	14	19	25
Temp.	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°
mm.	32	42	54	68	85	106	130	159	193	233
Temp.	60°	65°	70°	75°	80°	85°	90°			
cm.	28	33	39	47	54	63	73			

It attacks fat of all kinds as energetically as the chloride, and therefore the above valve was used (preceding abstract). For the determination of vapour pressure at temperatures above the normal, the device shown in the illustration was employed. *A* connects with a litre flask, which communicates with a long manometer and a pump for regulating the pressure of the atmosphere in the flask. *B* connects with the apparatus in which boron tribromide is distilled in a high vacuum, the bulb *D* being surrounded by liquid air. After collecting nearly 1 c.c. in *D*, the tubes are fused off at *E* and *F*, and the apparatus is placed in the thermostat nearly up to the tap *A*. When the mercury in *C* is steady, *A* is opened, and the pressure in the large flask is regulated until the columns at *C* are level again. *C* is therefore only a zero instrument, the actual pressure being read on the large manometer. J. C. W.



Boron Hydrides. V. Action of Chlorine and Bromine on B_2H_6 and $B_{10}H_{14}$. Valency of Boron. Alfred Stock, Ernst Kuss, and Otto Priess (*Ber.*, 1914, **47**, 3115—3149. Compare A. 1913, ii, 44, 699, 1053; 1914, ii, 359).—Previous work on the hydrides of boron introduced the difficulty that quadrivalence must be assigned to the element, at least in respect of its combinations with hydrogen. It was thought, therefore, that a study of

the action of halogens, on B_2H_6 especially, would throw some light on the question.

Some improvements in the preparation of the starting material, B_4H_{10}, are described. They consist chiefly in passing the crude gas through a tube at $-40°$, whereby white crystals of $B_{10}H_{14}$, m. p. 99·5°, are collected, then through a large U-tube at $-80°$, in which a little B_4H_{10}, some silicon hydride, and, chiefly, B_6H_{12}, are condensed, and finally the main bulk of the gas is condensed by cooling with liquid air. The yields obtained from 100 grams of "magnesium boride" were B_4H_{10}, 95 c.c. (0° and 760 mm.), and $B_{10}H_{14}$, 0·02 gram. The apparatus for the conversion of B_4H_{10} by heat into B_2H_6 was also improved, and the B_2H_6 which was pumped off from the liquid air condensation was condensed in a bath made by stirring liquid air into alcohol until the mass was almost solid. Such a bath maintains a temperature of $-125°$ to $-115°$ for some hours in a Dewar vessel.

The density of B_2H_6 was found to be 13·97. The gas condenses in needles when cooled slowly, and is not attacked by dry oxygen to any extent after some days at ordinary temperatures. Traces of moisture, however, decompose it at once, but hydrogen sulphide has no action, even at 100°. It inflames if the liquid is suddenly brought into the air (for example, when a breakage occurs).

The action of bromine and chlorine on the hydrides was the subject of a very exhaustive study. In the case of the solid, $B_{10}H_{14}$, the reaction was very sluggish, but replacement of hydrogen, and not addition, was the rule. Thus, the solid was left in a large excess of bromine for six months, when the residue, after evaporation, had a formula between $B_{10}H_{12}Br_2$ and $B_{10}H_{11}Br_3$, and apparent individuals were isolated by fractional crystallisation from a mixture of benzene and light petroleum. The alkaline solutions of these compounds reduced permanganate, and then yielded B_4H_{10} on acidifying. The acid solutions also reduced permanganate, and gradually evolved B_4H_{10}, and yet other, unknown, evil-smelling boron compounds.

The action of chlorine and bromine on B_2H_6 was studied in a series of elaborate experiments, which are described in minute detail, as future work will follow the same lines. Chlorine causes explosions at the ordinary temperature, whereas bromine reacts very slowly, even in the light, but completely in a few hours at 100°. In all the experiments, it was found that half of the halogen which is used is returned as the halogen hydride, in other words, substitution is the rule. Excess of halogen always leads to the unimolecular haloids BCl_3 and BBr_3, and not to B_2Cl_6 and B_2Br_6. This important fact led to an inquiry into the nature of the intermediate products involved in the transition of B_2H_6 into these haloids. The limited action of the halogens was therefore the chief subject of experiment, and it was the action of bromine that first afforded a clue to the problem. When B_2H_6 was treated with about one-third of the quantity of bromine required for complete reaction, the products were not the middle brominated compounds, like $B_2H_4Br_2$, but almost exclusively the extremes, B_2H_5Br

and BBr_3. The intermediate compounds were formed in small quantities, but they readily undergo rearrangement into the extremes, which was evidenced by the fact that the vapour pressures of the fractions soon increased at ordinary temperatures. Indeed, the monobromide, B_2H_5Br, also decomposes into B_2H_6 after a short time. The production of hydrogen bromide was never observed, and no evidence of the existence of $BHBr_2$, BH_2Br, $B_2H_2Br_4$, B_2HBr_5, and B_2Br_6 could be obtained. The reaction with chlorine followed the same course, but the intermediate compounds and B_2H_5Cl were far more volatile and labile than the bromides, and, consequently, the process was somewhat obscured.

Hence the action of halogens on an excess of B_2H_6 leads, first, to the production of such derivatives as $B_2H_4X_2$ and $B_2H_3X_3$, and then these speedily decompose and rearrange themselves into B_2H_5X and B_2H_6 on the one hand, and into BX_3 on the other.

The *monochloride*, B_2H_5Cl, is a spontaneously inflammable gas. The *monobromide*, B_2H_5Br, is a colourless gas with irritating odour. The following constants were observed; m. p. $-104°$, vapour pressure:

Temp.	$-80°$	$-70°$	$-60°$	$-50°$	$-40°$	$-36{\cdot}5°$	$-30°$	$-20°$	$-10°$	$-5°$
mm.	3	9	16	30	53	67	95	162	255	335

The b. p. would be about $+10°/760$ mm. It burns with a pale, greenish flame, and fumes in the air, owing to the reaction with water, $B_2H_5Br + 3H_2O = B_2O_3 + HBr + 5H_2$. It reacts immediately with potassium hydroxide, like B_2H_6, to form the hypoborate, $KOBH_3$ (A., 1914, ii, 359). It did not react with sodium, however, to any extent, and an attempt to convert it into B_4H_{10} failed.

These experiments prove that the highest, negative (hydrogen) valency of boron is four. The positive (oxygen, halogen) valency is three, although many substances have been described in which the valency is supposed to be five. These are reviewed, and the constitutions assigned to them are questioned. The most interesting are the oxychloride, $BOCl_3$ (Councler, 1878), and the sulphide, B_2S_5 (Moissan, 1892), of which nothing has been heard since the first mention of them. At any rate, boron does not obey the Bodländer-Abegg rule that the sum of the positive and negative valencies is eight (compare J. J. Thomson, A., 1914, ii, 450).

Many attempts have been made to obtain a hydride of boron with only one atom of boron in the molecule. Boron trialkyls exist, but are as unsaturated as triphenylmethyl, whilst the corresponding hydrides, BH_3 and CH_3, seem to be equally impossible of isolation. J. C. W.

Occurrence and Composition of Natural Gas. NIEDERSTADT (*Zeitsch. öffentl. Chem.*, 1914, **20**, 386—388).—Natural gas is found chiefly in the Caucasus and in North America, smaller quantities occurring in Denmark, England, Italy, Roumania, Russia, Spain, Austria-Hungary, and Germany. The gas consists principally of methane and its homologues, and the amount of unsaturated hydrocarbons rarely exceeds 1%. The American gas sometimes contains

a large quantity of hydrogen (up to 35%); carbon monoxide is not present in the gas found in any country, and many of the gases are free from carbon dioxide. The oxygen content is usually less than 1%. A gas of unusual composition is obtained from a deep boring in Pechelbronn, Alsace; it contains 47·75% of carbon dioxide, 46·17% of nitrogen, 5·65% of methane, 0·1% of oxygen, and 0·38% of helium (compare A., 1913, ii, 911). W. P. S.

Soluble Chlorides and Total Chlorine in Some English Cokes. STANLEY W. BRIDGE (*Analyst*, 1915, **40**, 143—146).—The following percentage quantities of soluble chlorides (as sodium chloride) were found in gas cokes obtained from coals of various origin: Derbyshire, 0·040 to 0·262; Durham, 0·013 to 0·122; Lancashire, 0·056; Yorkshire, 0·016 to 0·080; Flint (low temperature cannel residue), 0·357; Durham (metallurgical coke), 0·007. The amounts of total chlorine, expressed as percentages of sodium chloride, were: Derbyshire, 0·134 to 0·499; Durham, 0·039 to 0·344; Lancashire, 0·076; Yorkshire, 0·086 to 0·144; Flint, 0·918; metallurgical coke, 0·071. W. P. S.

Occurrence of Chlorine in Coal. A. DE WAELE (*Analyst*, 1915, **40**, 146—147).—Specimens of coal from the brine districts of the Midlands contained from 0·018 to 0·344% of chlorine, whilst Welsh coals were found to contain from 0·004 to 0·032%. As the quantity of chlorine found by ignition with calcium oxide agreed in every case with that found by extraction with hot water, it would appear that the whole of the chlorine was present in the coals in the form of soluble chlorides. Abnormal corrosion of boiler tubes, noticed when the Midland coals were used in the furnaces, was evidently caused by the presence of chlorine in some form in the furnace gases. W. P. S.

Preparation of Silicon Chlorides. GEOFFREY MARTIN (*Chem. News*, 1915, **111**, 208).—In reply to Kipping (this vol., ii, 165), the author states that his paper on the preparation of silicon chlorides (T., 1914, **105**, 2836) dealt solely with practical methods for the purpose; he claims priority for the suggested use of 50% ferrosilicon in the preparation. W. P. S.

Solubility of Mixtures of Sodium and Potassium Chlorides in Solutions of Hydrochloric Acid. W. B. HICKS (*J. Amer. Chem. Soc.*, 1915, **37**, 844—847).—The observation that potassium chloride is more soluble than sodium chloride in hydrochloric acid suggested that hydrochloric acid of constant b. p. might be of service in the commercial separation and purification of these salts. Determinations have now been made of the solubility of mixtures of the salts in hydrochloric acid of 8%, 17%, 20%, and 32% concentration at 25°. From the results of these determinations, and the values of the solubility of mixtures of sodium and potassium chloride in water obtained by Precht and Wittjen (A., 1881, 978), curves have been constructed showing the changes in solubility of the salts with variations in the concentration of the acid.

The solubility of both salts decreases rapidly as the concentration of the acid increases, but that of sodium chloride decreases at a greater rate than that of the potassium salt. The curves representing their solubilities intersect at a point, corresponding with 16·2% hydrochloric acid, where the solubility of each salt is 4·4%. As the acid becomes more concentrated, the saturated solution contains an increasingly larger proportion of the potassium salt, but in such strongly acid solutions the solubility of both salts is very small, the acid of constant b. p. (20·3% HCl) dissolving only 2·9% of potassium chloride and 2·2% of sodium chloride. It is evident, therefore, that hydrochloric acid is not suitable for effecting the commercial separation of these salts. E. G.

Preparation of Sodium Hypochlorite from the Hydroxide. U. Cattania and C. Ranucci (*Ann. Chim. Applicata*, 1915, **3**, 161—164).—Chlorine was passed into a 24% sodium hydroxide solution in a vessel standing in cold water, the liquid being kept well mixed. Samples were removed at intervals of ten minutes, and the percentages of active chlorine estimated both immediately and after the lapse of twenty-hours. It is found that stable products are obtained up to the time when deposition of sodium chloride begins, but that samples taken subsequently lose considerable proportions of their active chlorine in twenty-four hours. If this salt is removed from the liquid as it separates, the concentration of the active chlorine may be pushed to its utmost limit, provided that the alkalinity is maintained at about 0·5%. T. H. P.

The Double Salt of Sodium and Potassium Sulphates. Kichiro Okada (*Mem. Coll. Sci. Kyoto*, 1914, **1**, 95—103).—The equilibrium relationships in the system Na_2SO_4–K_2SO_4–H_2O have been investigated at 15°, 25°, 40°, 50°, 60°, 70°, and 80°. Mixtures of sodium and potassium sulphates in varying proportions were shaken with an equal weight of water for about twenty-four hours, and the composition of the saturated solution and of the residue determined by the tartrate method (this vol., ii, 373).

From the results, the conclusion is drawn that sodium and potassium sulphates form a double salt of the formula $K_3Na(SO_4)_2$. This double salt forms solid solutions with sodium sulphate, but not with potassium sulphate. The limits of existence of the solid solutions become more widely separated as the temperature rises from 15° to 60°, but approach one another between 60° and 80°. Up to 60°, the author's data are in accord with those obtained by Nacken (A., 1910, ii, 501), but this observer assumes that the solid solution field widens with rise of temperature up to 180°.

H. M. D.

Sodium Metasilicate Enneahydrate, a Well-defined, Crystalline Sodium Silicate. K. A. Vesterberg (*Zeitsch. anorg. Chem.*, 1914, **88**, 341—348. Compare A., 1913, ii, 406).—Sodium silicate solution with a large excess of sodium hydroxide will remain liquid for a long period in a closed vessel, but inoculation with the solid

salt produces crystallisation. The product is recrystallised several times from warm 2—3% sodium hydroxide solution, inoculating when cold. It is finally pressed between filter paper, and then has the composition $Na_2SiO_3,9H_2O$. The same salt is obtained when aqueous-alcoholic solutions are used. The crystals are rhombic.

The salt dissolves in water, with considerable absorption of heat. It melts completely at 48°, and loses $6H_2O$ slowly over sulphuric acid. The trihydrate yields a hexahydrate when kept over 25% sodium hydroxide solution. Complete dehydration only takes place at a high temperature. C. H. D.

Potassium Ammonoargentate. Edward C. Franklin (*J. Amer. Chem. Soc.*, 1915, **37**, 852—855).—During a study of the action of potassamide on solutions of silver salts in liquid ammonia (A., 1905, ii, 582), it was observed that silver amide dissolves readily in a solution of potassamide in this solvent. It has now been found that *potassium ammonoargentate*, $AgNHK,NH_3$ or $AgNH_2,KNH_2$, is produced in accordance with the equation $AgNH_2 + KNH_2 = AgNHK + NH_3$; it separates from concentrated solutions in crystals, which can be heated at 100° without change, but gradually undergo decomposition when left in the air. If the salt is treated with solutions of acids in liquid ammonia, silver amide is first precipitated, and dissolves, on further addition of the acid, with formation of the silver salt of the acid used. E. G.

Reaction Between Calcium Hydroxide and Sulphur in Aqueous Solution. S. J. M. Auld (T., 1915, **107**, 480—495).—The reaction between calcium hydroxide and sulphur under conditions precluding oxidation by contact with the atmosphere has been studied, using the specially constructed apparatus described in the paper. Calcium thiosulphate and calcium polysulphides (or oxysulphides) were the sole reaction products. Using an excess of sulphur, the ratio of total sulphur in solution as sulphide and polysulphides to sulphur as monosulphide was usually 4·5—5·0, but under certain conditions the existence of polysulphides as high as CaS_7 was indicated. Much of the sulphur of the higher polysulphides is loosely combined, and attempts were made by extracting, either from solution or from the dried solid, to obtain a lower stable polysulphide. The removal of sulphur in this way was continuous, due probably to a hydrolytic dissociation equilibrium of the type:

$$CaS_x + 2H_2O \rightleftharpoons Ca(OH)_2 + H_2S_x,$$
$$H_2S_x \rightleftharpoons H_2S + (x-1)S.$$

Nevertheless, a lower rate of extraction when the ratio above-mentioned was 1·6—2·3 points to the existence of a stable CaS_2 complex. Attempts to prepare this substance by boiling together lime and sulphur in the calculated proportions failed; in every case Herschell's crystals were obtained, for which the formula $CaO,CaS_2,7H_2O$ is proposed. It is suggested that the CaS_2 complex, probably in attachment to CaO, is the primary product of the action of lime on sulphur $[5Ca(OH)_2 + 6S = 2CaS_2,CaO +$

$CaS_2O_3+5H_2O$], and that the polysulphides also contain this complex, having the constitution $Ca<\begin{matrix}S\\ |\\ S\end{matrix}>S{:}S{:}S\ldots$, the sulphur atoms in the chain becoming progressively more loosely attached. The first addition of dilute hydrochloric acid to the polysulphide solution caused a precipitate or turbidity, which rapidly redissolved, and evidence was obtained that the resulting solution contained polysulphides of the order of CaS_7, although whether all the sulphur was actually thus chemically combined, or whether merely in solution, or whether the one condition gradually merges into the other, was left undetermined. G. F. M.

The General Behaviour of the Elements Sulphur, Selenium, and Tellurium in Sodium Calcium Silicate Glasses, with Special Reference to the Colours which they Produce. PIERO FENAROLI (*Kolloid. Zeitsch.*, 1915, **16**, 53—58. Compare A., 1914, ii, 728).—The colours produced by sulphur, selenium, and tellurium in sodium calcium silicate glasses can be interpreted in terms of the varying degree of dispersity of the element. In the case of sulphur, the coloration is due to molecular disperse sulphur present in the form of polysulphides, and there is no evidence of the presence of colloidal sulphur in glasses of this type.

In consequence of the more pronounced electro-positive character of selenium and tellurium, these elements have less tendency to form corresponding polyselenides and polytellurides, and glasses may readily be obtained in which the colour is due to elementary selenium or tellurium in colloidal form. The range of colour in presence of these elements is very much greater than in glasses coloured by sulphur, and the variations of colour are attributable to variations in the degree of dispersity of the selenium and tellurium. Glasses which contain molecular disperse selenium in the form of polyselenides have a chestnut-brown colour; those which contain colloidal selenium vary from yellow to reddish-violet. Glasses containing polytellurides are red in colour, whilst those in which the tellurium is present in the colloidal form exhibit colours which vary from reddish-brown to blue, according to the degree of dispersity. H. M. D.

A Chemical Explanation of the Anomalous Content of Water of Crystallisation of Cadmium Sulphate, $8/3H_2O$. C. BLOMBERG (*Zeitsch. anorg. Chem.*, 1915, **91**, 248—250).—In accordance with Noyes and Drucker's theory of complex ions, cadmium sulphate dissociates in concentrated solutions mainly thus:

$$3CdSO_4 \rightleftarrows [Cd_2SO_4]^{\cdot\cdot} + [Cd(SO_4)_2]''.$$

In the solid state, the three molecules combine, and are therefore capable of forming a hydrate containing a number of molecules which is not divisible by three. The same idea is applicable to other salts (compare this vol., ii, 139; Abegg and Bodländer, A., 1899, ii, 543). C. H. D.

Corrosion of Non-ferrous Alloys. CECIL H. DESCH (*J. Soc. Chem. Ind.*, 1915, **34**, 258—261).—An address delivered before the

Scottish section of the Society of Chemical Industry. An account is given of the results already described (A., 1914, ii, 367, 655), and of a permanent apparatus for the study of electrically stimulated corrosion. J. C. W.

Cerium-Magnesium Alloys. RUDOLF VOGEL (*Zeitsch. anorg. Chem.*, 1915, **91**, 277—298).—Cerium and magnesium may be melted together in a carbon vessel. Very thorough mixing is necessary, and the temperature must not rise above 900°.

The freezing-point curve has maxima at 738° and 780°, corresponding with the compounds CeMg and $CeMg_3$, and a break at 620°, corresponding with $CeMg_9$. A minute maximum at 632° is also inferred, due to a compound, Ce_4Mg. Solid solutions are only formed between CeMg and $CeMg_3$, whilst Ce_4Mg breaks up into Ce and CeMg at 497°. This is inferred from the microscopic structure, which is developed by heat-tinting.

Alloys corresponding with the compounds Ce_4Mg and CeMg are pyrophoric. CeMg is hard (H=5), and oxidises rapidly on heating. When containing magnesium in solid solution, the compound explodes violently in a Bunsen flame, the magnesium vapour being enclosed in a crust of oxide. Moist air at the ordinary temperature has very little action. $CeMg_3$ is still more stable towards air and acids, and is not pyrophoric. $CeMg_9$ is softer, and brittle. It falls spontaneously into fragments, which retain their silvery lustre, indicating some polymorphic change. C. H. D.

Fractional Crystallisation of the Picrates of the Rare Earths of the Didymium Group. L. M. DENNIS and F. H. RHODES (*J. Amer. Chem. Soc.*, 1915, **37**, 807—815).—Dennis and Bennett (A., 1912, ii, 257) have given an account of the fractional crystallisation of a mixture of the picrates of the metals of the didymium, erbium, and yttrium groups. It was observed that praseodymium and neodymium concentrated in the early fractions, but that a peculiar concentration of these metals occurred in the tenth and nineteenth fractions. The present work was undertaken with a view of investigating this abnormal behaviour.

A mixture of the picrates of the rare earths of the didymium group containing small quantities of those of the yttrium and erbium groups was subjected to forty-two series of fractional crystallisations. Praseodymium and neodymium concentrated in the least soluble fractions, yttrium in the most soluble fractions, and the metals of the erbium group in the intermediate fractions. Contrary to Dennis and Bennett's observation (*loc. cit.*), no indication was obtained of a concentration of neodymium or praseodymium in any fraction of intermediate solubility.

The results show that the fractional crystallisation of the picrates does not effect a separation of neodymium from praseodymium, but is a useful method for removing small quantities of metals of the erbium and yttrium groups from those of the didymium group, and also for separating yttrium from erbium and holmium. E. G.

Ammonobasic Aluminium Iodides. EDWARD C. FRANKLIN (*J. Amer. Chem. Soc.*, 1915, **37**, 847—852).—It has been observed (A., 1905, ii, 583) that, on adding potassamide to a solution of aluminium iodide in liquid ammonia, a precipitate is produced which is redissolved by an excess of potassamide. A further study of this reaction has now been made, with the following results.

When a concentrated solution of aluminium iodide in liquid ammonia is cooled to $-33°$, a mass of crystals of the salt, $AlI_3,20NH_3$, is produced, which melts at 8—13°, with separation of crystals of the composition $AlI_3,6NH_3$.

When potassamide is added to a solution of aluminium iodide in liquid ammonia, a white precipitate is formed, which redissolves on mixing the contents of the reaction tube. On continuing the addition of potassamide in quantity just insufficient to yield a permanent precipitate, a solution is obtained of an *ammonobasic aluminium iodide* in accordance with the equation

$$2AlI_3 + 3KNH_2 = Al(NH_2)_3,AlI_3 + 3KI.$$

At the ordinary temperature, this salt separates from solution in crystals containing $6NH_3$, whilst at low temperatures it separates in needles containing about $18NH_3$. On the addition of potassamide to a solution of this salt in liquid ammonia, an insoluble *ammonobasic aluminium iodide*, $Al(NH_2)_3,Al(NH_2)_2I,NH_3$, is precipitated, which, on being heated, loses 2 mols. of ammonia, with formation of the compound $Al(NH_2)_3,AlNHI$. E. G.

The Binary Systems Mn_2SiO_4–Ca_2SiO_4, Mn_2SiO_4–Mg_2SiO_4, and $MnSiO_3$–$FeSiO_3$. STEN KALLENBERG (*Zeitsch. anorg. Chem.*, 1914, **88**, 355—363).—The melting point is determined by Doelter's method with a heating microscope. Manganese and calcium orthosilicates form a continuous series of solid solutions, with a faint minimum near the manganese end. The density is proportional to the composition. The natural minerals glaucochroite and tephroite are members of this series. Glaucochroite occurs in nature in association with minerals which are not stable at the temperature of fusion.

Magnesium and manganese orthosilicates also form solid solutions, the density being proportional to the composition.

Manganese and ferrous metasilicates react readily with crucible materials, and measurements have not been obtained. C. H. D.

Change of Colour of Solutions of Cobalt Chloride. A. KOTSCHUBEI (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1055—1067).—The change in colour of cobalt chloride solutions from red to blue is favoured by increasing the concentration and by raising the temperature. On the assumption that the colour depends on the degree of hydration of the salt, it becomes necessary, therefore, to explain the variation of this hydration with the concentration and temperature. The hydration has been investigated by Nernst's method (A., 1901, ii, 12), which renders it possible to determine the quantity of water transmitted by the ions, and consequently combined chemically with them (compare Buchböck, A., 1906, ii,

519; Washburn, A., 1908, ii, 1009). For the non-electrolyte, mannitol and sucrose are inapplicable, owing to the difficulty of estimating them, the former not being separable from cobalt without alteration in weight, and solutions of the latter containing cobalt chloride being polarimetrically opaque; phenol is found to give satisfactory results, as it can be readily estimated, and does not interfere with the estimation of cobalt. A cathode of cobalt containing nickel and an anode of silver gauze were employed.

Experiments made with cobalt chloride solutions of various concentrations show that the hydration of the cobalt ions diminishes as the concentration of the salt increases (compare Bein, A., 1898, ii, 553). From his own results and those of previous investigators, the author draws the conclusion that the hydration of the cobalt ions and of the undissociated cobalt chloride molecules diminishes with increase of the concentration and with rise of temperature. It is probable that the change is from $[Co6(H_2O)_n]^{\cdot\cdot}$ to $[Co4(H_2O)_n]^{\cdot\cdot}$, $[Co4(H_2O)]^{\cdot\cdot}$, and $[Co(H_2O)_2Cl_2]$ and not to $CoCl_4''$. The decrease of the transference number of cobalt may be explained by the hydration of the ions (compare Riesenfeld and Reinhold, A., 1909, ii, 540). In blue alcoholic solutions of cobalt chloride, the colour is undoubtedly conditioned by the formation of complexes, such as $CoCl_2(Me\cdot OH)_2$, $CoCl_2(Et\cdot OH)_2$, $CoCl_4''$, etc. The formation of the ions $CoCl_4''$ as a result of the action of hydrochloric acid, and ammonium, potassium, sodium, glucinum, magnesium, calcium, strontium, and aluminium chlorides on aqueous cobalt chloride solutions, is not yet definitely established, but red solutions of cobalt chloride containing zinc, cadmium, antimony, mercuric or stannous chloride, form complex ions of the probable composition

$$\left[Co\begin{matrix}Cl_4\\(ZnCl_2)_2\end{matrix}\right]'', \left[Co\begin{matrix}Cl_4\\(HgCl_2)_2\end{matrix}\right]'', \text{ etc.}$$

T. H. P.

Tungsten and Tungsten-Chromium Compounds. V. K. Kantschev (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 729—742).—The following method of estimating tungsten gives exact results, and is far more rapid than that given by von Knorre (A., 1905, ii, 286). Excess of colourless benzidine hydrochloride solution is added to a hot solution of the tungstic compound, and the precipitate formed filtered off and washed with a small quantity of water. The filter and precipitate are mixed with water in an Erlenmeyer flask, and titrated at 60° with $N/10$-sodium hydroxide solution in presence of phenolphthalein, the contents of the flask being boiled when the end-point is approached in order to prevent the action of atmospheric carbon dioxide on the indicator. Since the benzidine tungstate is readily hydrolysed, the result of the titration gives the total tungstic acid.

Repeated attempts to prepare Lefort's ditungstates

$$(Na_2O,2WO_3+6H_2O)$$

and tritungstates $(Na_2O,3WO_3+4H_2O)$ (A., 1876, 278; 1879, 355,

600) resulted in failure, the paratungstate or a mixture of this with the metatungstate being always obtained.

Chromic tungstate, $Cr_2O_3,7WO_3+9H_2O$, is obtainable only when the violet modification of chromic chloride is employed. The compound obtained by Lefort from "sodium ditungstate" and chrome alum, and described as $Cr_2O_3,3WO_3+3H_2O$, consists of ordinary chromium paratungstate, $Cr_2O_3,7WO_3+16H_2O$. Further, the compounds to which Lefort ascribed the compositions $Cr_2O_3,4WO_3+6H_2O$ and $Cr_2O_3,5WO_3+5H_2O$ are respectively sodium paratungstate and a mixture of sodium para- and meta-tungstates, coloured green by admixtures of chromium compounds.

In a hot solution containing paratungstic acid and a chromic compound, the paratungstic acid exists, not in the free state, but as a tungsto-chromic acid, the greater proportion of the tungstic acid being incapable of precipitation by means of benzidine hydrochloride. T. H. P.

The Hydrates of Uranyl Nitrate and of Uranic Anhydride. R. DE FORCRAND (*Ann. Chim.*, 1915, [ix], **3**, 5—48).—For the most part a résumé of work already published (compare A., 1913, ii, 413, 477, 712). In the latter part of the paper, comparison is drawn between these results and those obtained for the oxide and nitrate of copper. For the heat of formation of copper nitrate, the author finds $Cu+N_2+3O_2=Cu(NO_3)_2(solid)+71{\cdot}49$ Cal., or $Cu(NO_3)_2aq(in\ the\ dissolved\ state)+81{\cdot}96$ Cal., values which are very close to those obtained for uranyl nitrate. W. G.

The Behaviour of Vanadium towards Silicon, Nickel, Copper and Silver, and of Boron towards Nickel. HANS GIEBELHAUSEN (*Zeitsch. anorg. Chem.*, 1915, **91**, 251—262).—Aluminothermic vanadium (94·2% V) reacts with silicon to form a compound, VSi_2, which melts at 1655°. The eutectic point at 1411° is near to the silicon end of the series. The curve has not been followed beyond 60% of vanadium. Solid solutions are not formed between silicon and the compound VSi_2. The latter crystallises in needles, and is harder than silicon.

Nickel and vanadium form a continuous series of solid solutions, within the range investigated, to 36% of vanadium. The freezing-point curve passes through a shallow minimum. The transformation temperature of nickel is rapidly lowered by vanadium.

Copper and vanadium, and silver and vanadium, are described as immiscible at 1800°.

Amorphous boron dissolves in molten nickel. The alloys have only been examined as far as 20% of boron. The freezing-point curve has maxima at 1225° and 1160°, corresponding with the compounds Ni_2B and Ni_3B_2 respectively, the latter of which undergoes a transformation at 1050°. A compound, NiB, is indicated at about 1020° without giving a maximum. The curve then rises rapidly, suggesting a maximum at the composition Ni_2B_3. Only the last of these compounds forms solid solutions. Only the alloys containing free nickel are magnetic. The compound Ni_2B is

slightly harder than quartz, whilst the compounds richer in boron are somewhat harder, but are scratched by topaz.

Amorphous boron is not dissolved, and hardly wetted, by molten copper, silver, thallium, bismuth, lead, or tin. It dissolves in calcium fluoride, and crystallises on cooling, but reacts violently with cadmium fluoride, forming boron fluoride and cadmium.

C. H. D.

Alloys of Bismuth and Cadmium. G. I. Petrenko and A. S. Fedorov (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 785—800).—In view of the discordant results obtained by different authors, the cooling curves of these alloys and their micro-structure have been investigated. At 140° the eutectic mixture crystallises, and the period of crystallisation at this temperature is greatest for the alloy containing 40% of cadmium, and gradually diminishes to zero for the pure metals. The micro-structures of the alloys are in agreement with the conclusions drawn from the cooling curves and the fusion diagram. Sections containing 0·5% of cadmium show crystals of bismuth surrounded by traces of finely granular eutectic. As the proportion of cadmium increases, the crystals of bismuth diminish, and the eutectic increases in amount until, with 40% of cadmium, almost pure eutectic is observed. This gradually gives way to crystals of cadmium as the percentage of the latter is increased still further.

Marked liquation occurs in these alloys. With those lying between pure bismuth and the eutectic concentration, the eutectic collects in the upper part, and the crystals of bismuth in the lower. With alloys between the eutectic concentration and cadmium, the latter is found at the top and the eutectic at the bottom. Thus, alloys containing a small proportion of either bismuth or cadmium are liable to be confused, since in either case the greater part of the section consists of homogeneous crystals, which may be regarded as mixed crystals, and taken to indicate the formation of solid solutions. Such liquation may, however, be largely avoided by careful mixing.

In general, the authors' results approximate to those of Portevin (*Rev. de Metall.*, 1907, **4**, 389), and indicate that bismuth and cadmium do not mix in the crystalline condition (compare Levin and Schottky, *Ferrum*, 1913, **10**, 192). T. H. P.

Atomic Weight of Tantalum. II. George W. Sears and Clarence W. Balke (*J. Amer. Chem. Soc.*, 1915, **37**, 833—844).—The determinations made hitherto of the atomic weight of tantalum have not given satisfactory agreement. Balke (A., 1910, ii, 962), from a study of the ratio $2TaCl_5 : Ta_2O_5$, obtained an average value $181·5 \pm 0·098$, whilst Chapin and Smith (A., 1911, ii, 899), from the ratio $2TaBr_5 : Ta_2O_5$, obtained $181·8 \pm 0·199$. Since in both these investigations a very pure salt was used, it seems that the principle involved must have been at fault. A

study has now been made of the ratios $2TaCl_5 : Ta_2O_5$ and $TaCl_5 : 5Ag$.

It has been found that the ignition and weighing of tantalum oxide obtained from the chloride cannot be employed for work requiring great accuracy, since tantalum oxide not only occludes nitric acid, but suffers slight loss on ignition.

An attempt to hydrolyse tantalum chloride, and precipitate the chlorine as silver chloride in presence of the tantalic acid, was found unsatisfactory, owing to the formation of an insoluble compound of silver with tantalic acid, probably a tantalate. Experiments to hydrolyse the tantalum chloride and distil off the hydrochloric acid gave discordant results, due to the retention of hydrogen chloride, which cannot be removed completely from tantalic acid by boiling with sulphuric acid, either under ordinary or reduced pressure. Other experiments showed that silver can be used to estimate hydrochloric acid in presence of tantalum fluoride if the precipitation is carried out in an approximately 5·5% solution of hydrofluoric acid, but three or four days are required for the establishment of equilibrium. Results obtained in this way gave values for the atomic weight of tantalum ranging from 180·90 to 181·36 (Cl = 35·46; Ag = 107·88). These results seem to indicate that tantalum chloride, purified by replacing the atmosphere of chlorine by dry air and distilling under either ordinary or reduced pressure, varies slightly in composition, due either to the occlusion of chlorine or to partial decomposition on distillation. E. G.

Formation of Colloidal Gold Solutions. F. HARTWAGNER (*Kolloid. Zeitsch.*, 1915, **16**, 79—80).—Experiments are described which show that sunlight, and to a smaller extent the light from a mercury arc lamp, have a very marked influence in promoting the formation of colloidal gold. Comparative observations were made on solutions containing gold chloride and various reducing agents, including hexamethylenetetramine, oxalic acid, ethyl alcohol, formaldehyde, acetaldehyde, and paracetaldehyde. A gold solution containing hydrogen peroxide was also found to exhibit a similar light effect.

Acetaldehyde is recommended as a substitute for formaldehyde in the preparation of stable ruby-red gold sols. With very dilute gold solutions, blue-coloured sols may be obtained by the action of sodium peroxide. H. M. D.

The Formation of Colloidal Solutions by means of Flames or Electric Spark Discharges. JULIUS DONAU (*Kolloid. Zeitsch.*, 1915, **16**, 81).—In agreement with the results obtained by Halle and Přibram (A., 1914, ii, 475), further experiments have shown that the production of colloidal gold by the action of a hydrogen flame on dilute solutions of gold salts is to be ascribed to the formation of nitrous acid. If, however, the hydrogen flame is allowed to play on the surface of water, to which a solution of gold chloride is subsequently added, a colloidal solution is not

obtained, but after some hours metallic gold is deposited. It is supposed that the difference in behaviour is due to the difference in the ion concentration of the liquid medium on which the flame acts. Red colloidal solutions of gold have also been obtained by the action of the spark discharge on very dilute solutions of gold chloride. The electrodes are brought into close proximity with the surface of the solution. In this case, also, the action is attributed to the formation of nitrous acid. H. M. D.

Gold–Cadmium Alloys. P. J. Saldau (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 994—1027).—The author has made a complete investigation of these alloys with reference to the electrical conductivity at temperatures up to 700°, the hardness, the peculiar properties of the eutectic alloys, the temperatures of crystallisation and transformation, the electromotive force, and the micro-structure. The results of the measurements are expressed in the form of tables and curves, and a number of photomicrographs are given. A special apparatus, comprising an electric furnace, has been devised for conductivity measurements on the solid alloys up to 700°, and would be applicable to the study of the dissociation of solid compounds, etc.

The results show that gold and cadmium form two compounds, AuCd and $AuCd_3$, giving solid solutions with their components within the limits 46—59 atom. % Cd for AuCd, and 74—79 atom. % Cd for $AuCd_3$. The mono-auride, AuCd, is characterised by Dalton points, both in its fusion diagram and in the isotherms of electrical conductivity and hardness. The diagrams of electrical conductivity and hardness for phases of variable composition, including the mono-auride, correspond perfectly with the theoretical diagrams for a definite chemical compound giving solid solutions with its components, the maximum of conductivity persisting at all temperatures from 25° to 600°. The supposed compound, Au_4Cd_3, described by Vogel (A., 1906, ii, 288), has no real existence, its composition merely corresponding with the limiting solid solution of the mono-auride with gold. Gold and AuCd, and cadmium and $AuCd_3$, form solid solutions containing, respectively, up to 35 atom. % of cadmium and 2 atom. % of gold.

Eutectic alloys of gold and cadmium in a condition of equilibrium differ markedly in their properties from the neighbouring alloys, exhibiting relatively great hardness and low values for the electrical conductivity and its temperature-coefficient and for the potential. Consequently, the existing schemes for the rectilinear expression of these properties are inapplicable to gold–cadmium alloys in the eutectic region, such alloys approximating in their properties to solid solutions. T. H. P.

Platinum in the Platiniferous Chromite of the Urals. A. del Campo y. Cerdan and S. Piña de Rubies (*Anal. Fis. Quim.*, 1915, **13**, 155—158).—The authors give a number of analyses of samples of platiniferous chromite from various parts of the Ural district. A. J. W.

Complex Compounds Containing Platinum and Hydrazine. L. TSCHUGAEV and M. GRIGORIEV (*Ber.*, 1914, **47**, 2446—2453).—Complex platinum compounds containing hydrazine are obtainable without difficulty if water is excluded (see also Tschugaev, A., 1914, i, 1054).

Hydrazine hydrate readily enters into action with Peyronne's chloride, $Pt(NH_3)_2Cl_2$, giving a solution, from which the addition of alcohol causes the separation of *α-platodiammine dihydrazine chloride*, $[Pt2NH_3,2N_2H_4]Cl_2$, colourless, prismatic crystals, which can be preserved for a few days, but gradually darken owing to liberation of platinum; the solution in water, which dissolves large quantities of the solid, decomposes much more rapidly. Other *salts* of the new complex were prepared by double decomposition of the chloride in concentrated aqueous solution with potassium iodide and with potassium platinochloride, the precipitate in the latter case being greenish. The addition of hydrochloric acid to an aqueous solution of the chloride causes the deposition of a much less soluble, crystalline *dihydrochloride*, $[Pt2NH_3,2N_2H_4]Cl_2,2HCl$, which, on treatment in aqueous solution with potassium platinochloride, gives a brownish-red precipitate of the *platinochloride*, $\left[(NH_3)_2Pt\begin{matrix}NH_2\cdot NH_2H\\NH_2\cdot NH_2\end{matrix}\right]_2(PtCl_4)_3$, and on boiling with diluted hydrochloric acid yields hydrazine hydrochloride and Peyronne's chloride.

From its chemical and general behaviour, the conclusion is drawn that the chloride, which constitutes the first new product above, is a *cis*-compound,

$$\left[\begin{matrix}NH_3\\NH_3\end{matrix}\!>\!Pt\!<\!\begin{matrix}NH_2\cdot NH_2\\NH_2\cdot NH_2\end{matrix}\right]Cl_2,$$

whilst to the derived dihydrochloride the structure

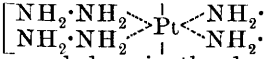
$$\left[\begin{matrix}NH_3\\NH_3\end{matrix}\!>\!Pt\!<\!\begin{matrix}NH_2\cdot NH_2\cdot H\\NH_2\cdot NH_2\cdot H\end{matrix}\right]Cl_4$$

is assigned.

The *trans*-isomeride of the above chloride, namely, *β-platodiammine dihydrazine chloride*, $\left[\begin{matrix}NH_3\\NH_2\cdot NH_2\end{matrix}\!>\!Pt\!<\!\begin{matrix}NH_2\cdot NH_2\\NH_3\end{matrix}\right]Cl_2$, is obtained in a similar manner to the α-isomeride from hydrazine hydrate and the chloride of Reiset's first base; it forms microscopic, colourless needles, and is more stable and less soluble than the *cis*-compound, which it resembles in giving a precipitate with potassium iodide solution; the precipitate obtained with potassium platinochloride, however, is red, but soon darkens. The *trans*-chloride also combines with hydrochloric acid, forming a stable and quite distinct *dihydrochloride*.

By the action of hydrazine hydrate on tripropylammonium platinochloride in chloroform solution, as also by interaction of hydrazine hydrate, and such substances as $[Pt(SEt\cdot C_2H_4\cdot SEt)Cl_2]$ or of the type $[Pt2(R_2S)Cl_2]$ (compare Tschugaev and Subbotin, A., 1910, i, 354), there can be obtained *platotetrahydrazine chloride*, $[Pt4N_2H_4]Cl_2$, microscopic needles or prisms very soluble

in water. The chloride, to which is ascribed the structure



can be kept for several days in the dry condition, but decomposes more rapidly in aqueous solution, especially on the addition of alkali, with effervescence and liberation of platinum. With sodium iodide solution, the chloride gives a precipitate of the *iodide*, $[Pt(N_2H_4)_4]I_2$ (silky needles), whilst potassium platinochloride solution produces a flesh-coloured precipitate.

D. F. T.

Mineralogical Chemistry.

Conditions of Natural Gas in the Earth's Strata. GEORGE A. BURRELL (*J. Ind. Eng. Chem.*, 1915, **7**, 322—324).—Taking into consideration the composition of natural gases, the pressures and temperatures that prevail in natural gas strata, and the temperatures and pressures that are necessary for the liquefaction of the gaseous paraffin hydrocarbons, it is evident that such a natural gas as that found at Pittsburgh, U.S.A., can never occur in the strata in liquid form. This conclusion does not apply in cases where the gases are closely associated under heavy pressure with oil in the sands; under such condition there is a solution of the gases in the oil. W. P. S.

Grahamite from Kunda, Esthonia. BRUNO DOSS (*Centr. Min.*, 1914, 609—615).—An asphaltum occurring in Silurian limestone at this locality has a columnar structure and pitch-black colour; it is brittle, with a splintery fracture, and the powder is brown; H = 2, $D^{18\cdot2}$ 1·111 (1·110—1·160). Analysis by S. BLUMENFELD gave.

C.	H.	S.	N.	O H_2O.	Ash.
83·28	8·53	2·16	1·51	3·81	0·71

The material resembles American grahamite, but it differs from this in the brown colour of its powder and in its greater solubility in oil of turpentine (71% being soluble) and in chloroform (97% soluble); the name *kundaite* is therefore suggested. L. J. S.

The Origin of Hard Salt and the Secondary Transformations of Stassfurt Salts in Relation to van't Hoff's Equilibrium Diagrams. M. RÓZSA (*Zeitsch. anorg. Chem.*, 1915, **91**, 299—319. Compare A., 1914, ii, 376).—The following salts may occur in the deposits either as products of primary crystallisation or as the result of secondary transformations: anhydrite, polyhalite, kieserite, carnallite, and sylvite. The following occur only as products of secondary origin: kainite, schœnite, leonite, blödite,

reichardite, pinnoite, langbeinite, lœweite, vanthoffite, and glaserite. Their formation has occurred under widely varying conditions of temperature, but the observed discontinuities of crystallisation may be accounted for by a comparison with van't Hoff's equilibrium diagrams for different temperatures. A continuous desiccation at a temperature above 72°, as the origin of hard salt, is unlikely, and the effect of pressure and circulation of solution in different directions must be taken into account. The temperatures of transformation are discussed in detail. C. H. D.

Transformations of the Potassium and Magnesium Salts in the Salt Deposits of the Werra Region. M. Rózsa (*Zeitsch. anorg. Chem.*, 1914, **88**, 321—332. Compare A., 1914, ii, 376).—The Werra deposits differ from those of Stassfurt in having two isolated layers of potassium and magnesium salts between three thick beds of rock salt. The arrangement of the layers is complex, and is illustrated in the paper by profiles. Periodic strata of halite–carnallite are often observed. The deposits can in many cases only be accounted for by the secondary action of percolating water, leading to a series of changes which is the reverse of that represented in van't Hoff's diagrams. The principal secondary transformations recorded are those of halite–carnallite into halite–sylvite and sylvite–halite–carnallite, of halite–sylvite into halite–carnallite, of sylvite and kieserite into langbeinite, of hard salt into thanite (halite–kainite), of anhydrite and carnallite or kieserite into polyhalite, and of sylvite–halite, kieserite and anhydrite into thanite–polyhalite. C. H. D.

The Fluorite-Yttrofluorite Group. Thorolf Vogt (*Jahrb. Min.*, 1914, ii, 9—15).—Mixtures of fluorite (m. p. 1384°) and yttrium fluoride fused together give cubic mixed crystals up to about 50% YF_3; there is a maximum m. p. at 1408° with 20% YF_3, corresponding with $7CaF_2,YF_3$, or nearly the same as the mineral yttrofluorite, $20CaF_2,7YF_3$ (A., 1911, ii, 733). When more than 50% YF_3 is present, hexagonal crystals (optically uniaxial with low negative birefringence) separate in addition to the cubic crystals. Pure yttrium fluoride yields optically biaxial crystals. Mixtures of calcium and cerium fluorides give cubic mixed crystals up to 55·8% CeF_3; these are referred to as cerfluorite, and, mixed with yttrofluorite, they find a representative in the mineral yttrocerite. L. J. S.

Constitution of Zinc-blende, Wurtzite, and Hauerite. A. Beutell and M. Matzke (*Centr. Min.*, 1915, 263—272).—The following materials were used in the experiments: I blende from Laurenburg, Nassau; II blende from Picos de Europa, Spain; III wurtzite from Przibram, Bohemia; IV wurtzite from Albergaria velha, Portugal. These analyses all lead exactly to the ratio R : S = 1 : 1, thus disposing of the suggestion of J. Weber (A., 1908, ii, 302) that blende and wurtzite differ slightly in composi-

tion. The silver-plate test (A., 1914, ii, 136) shows the presence of free sulphur in none of the minerals.

	Zn.	S.	Fe.	Pb.	Cu.	Sn.	Cd.	Insol.	Total.
I.	65·38	32·75	0·90	0·36	0·35	0·05	—	0·16	99·95
II.	65·44	33·38	0·40	—	—	0·45	—	—	99·67
III.	62·64	32·10	2·43	0·41	—	—	1·84	0·30	99·72
IV.	59·70	32·90	6·02	0·15	—	—	1·07	0·13	99·97

Blende, when slowly oxidised (in a dilute solution of hydrogen peroxide in the presence of air and sodium carbonate, or sodium acetate and acetic acid), gives rise to a separation of half of the sulphur, and the other half is oxidised to sulphuric acid, whilst with wurtzite all the sulphur is oxidised to sulphuric acid. The formula of blende is therefore written Zn_2S_2.

Wurtzite (anal. V of material from Raddusa, Sicily), when shaken with water and air, is oxidised, with the separation of free sulphur, no sulphuric acid being formed. The mineral thus behaves differently from pyrites, and it is consequently regarded as not belonging to the pyrites group.

	Mn.	Fe.	S.	SiO_2.	Total.
V.	46·47	0·03	53·27	0·16	99·93

L. J. S.

Cobaltnickelpyrite. V. J. Vernadski (*Centr. Min.*, 1914, 494—496).—This name, recently proposed by Henglein (A., 1914, ii, 282), had previously been used by the author in his Russian text-book on mineralogy (1910) for pyrites containing 2·0—3·5% Co and 2·2—5·8% Ni. These minerals may be identical; but it is possible that Henglein's material represents $(Co,Ni,Fe)S_2$ mechanically intermixed with some ordinary pyrites, rather than $(Fe,Co,Ni)S_2$, in which case a distinctive name would be advisable.

L. J. S.

An Occurrence of Grahnite in Pegmatite in Finland. Penhti Eskola (*Jahrb. Min.*, 1914, ii, Ref. 184; from *Geol. För. Förh.*, 1914, **36**, 25—30).—Strings of metallic sulphides (zinc blende, pyrrhotite, iron pyrites, and copper pyrites) occur in pegmatite veins, and in the gneiss which these veins traverse near Traskböle, in the parish of Perniö, Finland. In the pegmatite, these strings are surrounded by quartz, and in this, as well as in the adjacent pegmatite, the gahnite is found as large grains, and rarely as octahedral crystals. This mineral owes its origin to the pegmatites having broken through pre-existing mineral veins, and taking up zinc in the fused mass. The gahnite, D 4·478, gave on analysis.

Al_2O_3.	Fe_2O_3.	FeO.	ZnO.	NiO.	MnO.	MgO.	SiO_2.	TiO_2.	H_2O.	Total.
55·74	0·90	11·73	27·98	0·02	0·22	1·64	1·64	trace	0·16	100·03

L. J. S.

Alteration of Crystal Angles with Change of Temperature in Isomorphous Groups. F. Rinne (*Centr. Min.*, 1914, 705—718).—The change in angles over a range of temperature from −170°

to +600° was determined for various members of the rhombohedral carbonates and plagioclase groups, and the results plotted on curves and compared. The cleavage angle of calcite (Iceland spar) changes from 74°44′11″ at −165° to 75°53′31″ at 596°. Other members of this group examined in detail include dolomite from Sterzing, Tyrol (anal. I), chalybite from East Pool Mine, Cornwall (II), and rhodochrosite from Diez, in Nassau (III; other portions of the same specimen gave up to 10% $FeCO_3$).

	$CaCO_3$.	$MgCO_3$.	$FeCO_3$.	$MnCO_3$.	Insol.	Total.
I.	49·62	45·39	4·98	—	—	99·99
II.	—	0·69	96·34	2·52	—	99·55
III.	—	—	1·79	97·83	0·61	100·23

For albite, the cleavage angle (001):(010) ranges from 93°40′21″ at −170° to 93°6′6″ at 594°; somewhat similar results were obtained with anorthite and labradorite. L. J. S.

The So-called Lublinite, a Supposed New Modification of Calcium Carbonate. O. Mügge (*Centr. Min.*, 1914, 673—675. Compare A., 1914, ii, 665).—From a microscopical examination of "rock-milk" from Adams Valley, near Brünn, the conclusion is drawn that there is no occasion to assume the existence of a new (monoclinic) modification of calcium carbonate. The needles retain their form at a temperature of 430°. Curved forms are perhaps pseudomorphous after organic remains. The material is doubtless only calcite, except a small portion which is insoluble in dilute acetic acid, and this is perhaps dolomite. L. J. S.

"Hammer-stones." Tadasu Hiki (*Mem. Coll. Engin. Kyoto*, 1915, **1**, 55—58).—Pseudomorphous crystals similar to those known as pseudogaylussite (A., 1902, ii, 89), jarrowite, thinolite, and glendonite, occur abundantly in shales of Tertiary age in the province Shinano, and at several other localities, in Japan. They have a prismatic or pyramidal form with rhombic cross-section, and rough, brown surfaces; the internal structure is granular. Analysis gave.

CaO.	Fe_2O_3.	Al_2O_3.	MgO.	Fe_2O_3.	CO_2.	SiO_2.
52·33	3·44	1·00	0·48	3·44	37·00	0·64

L. J. S.

Composition of the Pyromorphites. M. Amadori and E. Viterbi (*Mem. Accad. Lincei*, 1914, [v], **10**, 386—408).—Twenty specimens of pyromorphite of diverse origins have been analysed. The specific gravity varies only between 7·06 and 7·12, these limits being far closer than those given by Dana ("A System of Mineralogy," 1909, 770), namely, 6·5 and 7·1. The greater or less proportion of arsenate occurring in the pyromorphites does not alter the specific gravity sensibly, the value for the chloro-arsenate or mimetite being 7·0—7·25, and the content of calcium is too small to produce appreciable variation. Most of the specimens

examined contain arsenic, and all show the presence of calcium, but the proportions of the latter element found are probably higher than those really present, owing to the protracted manipulation necessarily preceding the estimation. The value of the ratio, RO_4 : Cl, varies between 2·95 and 3·04, the small deviations from the value 3 being due, undoubtedly, to experimental error in the estimations. Thus, all the specimens examined have the composition $MCl_2,3M_3(PO_4)_2$, and the divergent results obtained by previous investigators appear to result from imperfect analytical methods or from faulty preparation of the material analysed; the low values often given for the percentage of chlorine are probably caused by dissolution of the mineral in the warm.

Pyromorphites of slightly different composition may occur in one and the same locality, and variations are also found between the compositions of the outer and inner layers of a single crystal. With two specimens from Wheal Alfred, in one case the inner, and in the other the outer, portions contained the more arsenic.

T. H. P.

Löwigite and other Minerals from near Mt. Kinzhal, Caucasus. V. V. Arshinov (*Jahrb. Min.*, 1914, ii, Ref. 362; from *Petrogr. Inst. "Lithogaea," Moscow, Publication* No. 3, 1913, 1—11).—Small white nodules and reniform masses occurring in sedimentary rocks (marly shale with gypsum) near trachy-liparite in the district of the Pyatigorsk mineral springs have D 2·67 and the composition $2(K,Na)_2O,6Al_2O_3,7SO_3,15H_2O$, as given by the following analysis made on material dried at 110°. The mineral is thus an impure löwigite, and is a product of solfataric action.

Al_2O_3.	Fe_2O_3(FeO).	K_2O.	Na_2O.	Li_2O.	SO_3.	C.	CO_2.	H_2O.	Total.
36·87	0·44	5·07	3·93	0·16	34·76	0·53	0·06	16·67	99·75*

* Including: MnO,CaO,CuO,NiO, 0·19; SiO_2, 0·69; Insol. 0·60.

Analyses are also given of an alteration product of felspar from the trachy-liparite, and of a phosphatic cave deposit. L. J. S.

The Supposed Vanadic Acid from Lake Superior is Copper Oxide. Waldemar T. Schaller (*Amer. J. Sci.*, 1915, [iv], **39**, 404—406).—According to Teschemacher (*ibid.*, 1851, [ii], **11**, 233), the yellow substance sometimes found as an incrustation on the surface of the native copper from the Cliff Mine is vanadic acid (VO_3). A specimen examined by the author was found to consist of cuprous oxide, and it is suggested that the mineral is a variety of cuprite, or possibly hydrocuprite. H. M. D.

Compounds of Easily and Difficultly Volatile Components, with Especial Reference to Mineralogenetic Problems. Paul Niggli (*Jahrb. Min.*, 1914, ii, 69—99).—Systems such as $CaO–CO_2$ and rock-forming silicates with water afford special cases of Roozeboom's types of the formation of mixed crystals. Four such types, embracing solid, liquid, and gaseous phases, are studied in detail and illustrated by equilibrium diagrams and formulæ, and

their application to the formation of hydrated silicates, especially those of pneumatolytic origin, are discussed. L. J. S.

Mineral Syntheses. C. DOELTER (*Jahrb. Min*, 1914, ii, Ref. 179—180, 346—347; from *Sitzungsber. Akad. Wiss. Wien, Math.-naturw. Kl.*, 1913, **122**, 3—20, and *Tsch. Min. Petr. Mitt.*, 1913, **32**, 129—132).—*Phenakite* crystals were obtained by fusing silica with five parts of hydrated glucinum nitrate, some ammonium fluoride being added to lower the temperature of fusion. Crystals, probably identical with *euclase*, were obtained from a mixture of glucinum carbonate, alumina, and silica in the proportions required by the euclase formula; the material was heated between layers of sodium fluoride in a porous magnesia crucible, but the mass only sintered. *Leucophane* crystals separated from a mobile fusion of glucinum carbonate, calcium carbonate, and silica, with sodium hydrogen fluoride. Magnesium metasilicate, when fused, gives a mixture of enstatite and clinoenstatite; between these there appears to be no definite transformation point. Attempts to prepare chrome-diopside synthetically were without success.

L. J. S.

Nephrite in situ in the Southern Apennines. S. MARTIUS (*Jahrb. Min.*, 1914, ii, 1—8).—Nephrite occurs as veins in serpentine near the contact of the latter with gabbro at Episcopia, in Basilicata (anal. I), and on Monte Brancato, near Latronico (anal. II).

	SiO_2.	TiO_2.	Fe_2O_3.	FeO.	Al_2O_3.	CaO.	MgO.	CO_2.	H_2O.	Total.	Sp. gr.
I.	56·48	trace	0·98	3·15	0·43 (?)	11·62	23·26	—	4·27	100·19	2·99
II.	56·83	—	1·46	2·72	trace	12·26	22·51	0·50	3·53*	99·81	3·06

* H_2O below 110°, 0·28, H_2O at 110—1250°, 3·25%.

Deducting ferric oxide as magnetite, and combining the remainder of the ferrous oxide with the magnesia, these analyses give the ratios of SiO_2: CaO: MgO as 4·5: 1: 2·9 and 4·3: 1: 2·7 respectively, instead of 4: 1: 3, as required by the actinolite formula. The material is, however, somewhat impure, owing to admixed chlorite and serpentine.

A summary of the several views as to the origin of nephrite is given. In the present instances, the nephrite veins have probably emanated from the gabbro, although some of the material may have been derived from the peridotite which gave rise to the serpentine. All the rocks are highly contorted. L. J. S.

Chemical Disintegration of Talc, Chlorite, and Biotite. FRITZ MALT (*Jahrb. Min.*, 1914, ii, Ref. 357—359; from *Inaug.-Diss.*, Leipzig, 1913, 1—37).—The minerals examined were: pale greenish-white talc from Greiner, Tyrol (anal. I); pale green chlorite from Slatoust, Urals (II); and biotite (anomite) from Miask, Urals (III).

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
I.	61·56	—	—	—	2·72	30·46	—	—	5·21	99·95
II.	39·64	—	10·52	2·44	1·31	32·07	—	—	13·95	99·93
III.	37·66	1·75	21·97	3·29	14·14	14·15	4·18	0·65	2·99	100·78

Talc loses most of its water at a red heat; there is a break in the dehydration curve at 850—960°. The ignited material consists of enstatite and silica. Hydrochloric, nitric, and sulphuric acids have only a very slight action on talc; fusion with salt of phosphorus leaves a residue containing 97·45% silica (tridymite?). Chlorite loses water gradually up to 460°, with a break up to 560°, above which water is again gradually lost, the bulk being lost at red heat. Digested with dilute sulphuric acid or with strong hydrochloric acid, the mineral leaves a residue of hydrated silica. Biotite is bleached by digestion with hydrochloric acid, leaving scales of hydrated silica, which are optically negative and nearly uniaxial. With hydrogen fluoride, the silica is expelled, leaving white scales, composed of fluorides of aluminium, iron, and magnesium. Various experiments were also made on the baueritisation (A., 1913, ii, 868) of biotite. L. J. S.

The System Anorthite–Forsterite–Silicia. Olaf Andersen (*Amer. J. Sci.*, 1915, [iv], **39**, 407—454).—Preliminary experiments according to the methods described previously (compare Shepherd, Rankin and Wright, A., 1911, ii, 725; this vol., ii, 50) showed that in certain mixtures, anorthite ($CaO,Al_2O_3,2SiO_2$) reacts with forsterite (Mg_2SiO_4) to form spinel ($MgAl_2O_4$), which separates out as the primary solid phase. The complete equilibrium relations of the above system can therefore only be dealt with by treating it as a part of the quaternary system

$$CaO–MgO–Al_2O_3–SiO_2.$$

The present paper deals with that portion of the quaternary system in which the composition of the mixtures can be expressed in terms of the components anorthite–forsterite–silica. Excepting the relatively small spinel region, this can be treated as a ternary system, and the experimental data are actually considered from this point of view.

The general character of the true ternary part of the equilibrium diagram is that of a system with no ternary compound, one binary compound ($MgSiO_3$), which is unstable at its melting point, and two quintuple points, one of which is a ternary eutectic with anorthite, clino-enstatite and tridymite as solid phases, and the other a transition point with anorthite, forsterite, and clino-enstatite as solid phases. The ternary eutectic temperature is 1222±2°, and the composition anorthite 50·5%, forsterite 16·5%, silica 33·0%. The transition point is at 1260±2°, and the composition of the liquid phase anorthite 55%, forsterite 25·5%, silica 19·5%.

The crystallisation curves in different sections of the diagram are discussed, and it is shown that conclusions may be drawn which have a direct bearing on the crystallisation of olivine- and pyroxene-bearing rocks. H. M. D.

Ussingite, a New Mineral from Kangerdluarsuk, Greenland. O. B. Böggild (*Jahrb. Min.*, 1914, ii, Ref. 202—203; from *Meddelelser om Grönland*, 1914, **51**, 103—110, and *Zeitsch. Kryst. Min.*, 1914, **54**, 120—126).—This is violet-red, with three directions of

cleavage. On the best (basal) cleavage the lustre is pearly, elsewhere it is vitreous. The cleavage angles ($cm = 70°21'$, $cM = 71°30'$, $mM = 90°28'$) and the optical orientation point to triclinic symmetry. Refractive indices low ($\alpha = 1{\cdot}5037$, $\beta = 1{\cdot}5082$, $\gamma = 1{\cdot}5454$), H 6—7, D 2·495. Analysis by C. Christensen gives the formula $HNa_2Al(SiO_3)_3$. When heated, the mineral fuses readily, with violent intumescence; it, however, contains less water than the zeolites, and also differs from these in its mode of occurrence. Only three specimens, as loose blocks, have been found; the minerals (ægirite, sodalite, felspar) attached to these indicate that the mineral was derived from the pegmatite veins traversing the sodalite-syenite of the district.

SiO_2.	Al_2O_3.	Na_2O.	H_2O.	Total.
58·74	17·73	19·91	4·19	100·57

L. J. S.

Zeolites from Kara-Dagh, Crimea. P. N. Tschirvinski and A. Orloff (*Jahrb. Min.*, 1914, ii, Ref. 360—361; from *Ann. Géol. Min. Russie*, 1913, **15**, 144—148).—Analcite, D 2·214. anal. I. Mesolite as white to rose-red radiating masses, II. Heulandite, reddish-brown, owing to enclosed iron oxide, III. Apophyllite, IV.

	SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	Na_2O.	K_2O.	H_2O.	F.	Total.
I.	56·53	22·30	—	—	—	13·06	trace	8·67	—	100·56
II.	46·20	26·33	—	—	13·57	4·12	0·03	11·18	—	101·43
III.	59·08	11·70	6·29	0·05	9·83	—	0·52	13·46	—	100·93
IV.	55·14	—	—	—	22·35	1·17	3·21	17·19	1·78	100·84

L. J. S.

Pseudomorphs after Orthoclase from the Tirschenreuth Granite. Laura Hezner (*Centr. Min.*, 1914, 607—608).—Large porphyritic crystals of orthoclase in the granite of Tirschenreuth, in the Bavarian Upper Palatinate, are in places altered to a green-blue-grey, compact (but with earthy aspect) material, which has the composition given below. H 3—4, D 2·55. The associated biotite is partly bleached and altered to chlorite, and this mineral may have supplied the magnesia to the pseudomorphs. Under the microscope, the pseudomorphous material is seen to consist of a mixture of chlorite and very fine, colourless scales, which appear to be sericite and kaolinite. The phosphoric acid is present as apatite.

SiO_2.	TiO_2.	P_2O_5.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
54·80	trace	0·20	21·88	3·57	1·18	0·02	0·54	6·41	5·95	0·65	5·38	100·58

L. J. S.

The Mineral Rumpfite. Karl A. Redlich (*Centr. Min.*, 1914, 737—740).—A new analysis and the optical characters of the original rumpfite from Jassing, near St. Michael, in Upper Styria, has recently led Tschermak (*Tsch. Min. Petr. Mitt.*, 1914, **32**, 542)

to the conclusion that this mineral is identical with clinochlore. This new analysis (I) by T. PANZER differs widely from that of G. Firtsch (1890) in the amounts of alumina and magnesia, the excess of alumina in the older analysis being perhaps partly due to the presence of admixed sericite.

Analyses by O. GROSSPIETSCH (II, IV, VI) and H. PRASCHIL (III, V, VII) are also given of rumpfite from Eichberg on the Semmering Pass (II and III), from Veitsch in Styria (IV and V), and from Häuselberg, near Leoben (VI and VII). Analyses I—V agree with the Tschermak chlorite formula Sp_2At_3, as for chinochore, whilst VI and VII are nearer to Sp_3At_7.

	SiO_2	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	K_2O.	Na_2O.	H_2O.	CO_2.	Total.
I.	31·31	20·07	0·82	1·36	33·30	—	0·85	0·39	12·87	—	100·97
II.	30·40	21·41	1·24	0·91	33·54	trace	0·76	0·20	12·33	—	100·61
III.	29·85	20·57	1·19	0·76	34·01	trace	0·7	0·28	12·72	0·62	100·07
IV.	30·08	20·48	1·76	2·33	33·03	trace	n.d.	n.d.	12·41	—	—
V.	29·79	20·40	2·86	1·25	32·55	trace	trace	0·58	12·82	0·09	100·34
VI	28·18	22·31	1·54	9·34	25·09	0·46	0·39	0·24	12·67	—	100·22
VII.	27·93	23·51	2·50	8·39	26·19	trace	0·27	0·43	11·72	0·15	100·99

L. J. S.

Riebeckite from Gloggnitz, Lower Austria. A. SCHIERL (*Centr. Min.*, 1914, 604—607).—An amphibole with the optical characters of riebeckite occurs in the troctolite (forellenstein) near Gloggnitz. Analysis I is of bluish-grey material intermixed with some magnetite, II of bluish-black material with magnetite and hæmatite, and III of bluish, fibrous material. Other analyses of less pure material are also given. D 3·33. Direct determinations of the alkalis (mainly soda) gave 2—5%. The mineral is a ferrous ferric silicate, and represents a riebeckite poor in soda:

	SiO_2.	Fe_2O_3(+FeO).	Al_2O_3.	MnO.	CaO.	MgO.	H_2O.	Na_2O.	P_2O_5.
I.	54·40	40·06	1·83	0·81	1·26	0·34	0·98	[0·32]	trace
II.	52·71	42·72	1·68	1·19	0·70	0·14	0·51	[0·35]	—
III.	53·79	41·26	2·01	0·89	0·76	0·30	0·55	[0·44]	trace

L. J. S.

Analytical Chemistry.

A Convenient and Exact Method of Working with Pipettes. GEORG TH. PANOPULOS (*Chem. Zeit.*, 1915, **39**, 248).—The measurement of liquids with a pipette is much facilitated by fitting a short piece of thin rubber tubing and a glass mouthpiece on the upper end. A glass bead of suitable size is placed inside the rubber tubing, and by pulling the latter slightly with the fingers an air passage is made, and the pipette can be filled, whilst the moment it is released it sits firmly round the bead and prevents

the liquid running out. A very fine regulation of the drops is thus obtained, and a pipette graduated in cubic centimetres can be utilised as a small, accurate reading burette if desired.

G. F. M.

A Pipette for Gas Analyses which permits a Circulation of the Reagent within the Pipette. GEORG WEMPE (*Zeitsch. angew. Chem.*, 1914, **27**, 584).—The apparatus consists of an absorption chamber filled with glass beads, and connected from the base, through a tap, with two bulbs. The lower one is provided with a side-tube, and is joined to the upper by a tube which extends inwards to the bottom, so that liquid in this bulb can be driven into the upper bulb by applying air pressure with a rubber ball, or otherwise, at the side-tube. The upper bulb is provided at its base with a tube leading back to the top of the absorption chamber. In use, the gas is passed into the latter in the usual way, driving the absorbing liquid into the lower bulb. The tap is then closed, and the liquid pumped into the upper bulb, whence it is allowed to run back into the absorption chamber by again opening the tap. The liquid passing into the lower bulb is again pumped into the upper one, and the circulation thus continued until absorption is complete. G. F. M.

A Simple Hydrogen Electrode. HENDRIK PIETER BARENDRECHT (*Biochem. J.*, 1915, **9**, 66—70).—A simple arrangement for the estimation of the true reaction of liquids is described; it remains always ready for use. It is in some ways an improvement on Walpole's electrometric titrating apparatus, and suitable for the open bench, special provision being made for allowing instantaneous and accurate estimations even in liquids which contain carbon dioxide and oxygen. W. D. H.

Detection of Hydrochloric Acid in Medical Practice. JOHANNE CHRISTIANSEN (*Zeitsch. Biol.*, 1914, **64**, 549—553. Compare A., 1912, ii, 1187; 1913, i, 112).—Polemical against Krummacher (A., 1914, ii, 214). The author maintains that Günzberg's reagent is a specific indicator for free strong acids. H. W. B.

Detection of Hydrochloric Acid in Medical Practice. O. KRUMMACHER (*Zeitsch. Biol.*, 1914, **64**, 554—558).—A reply to Christiansen (preceding abstract). H. W. B.

Qualitative Detection and Quantitative Estimation of Halogens in Organic Compounds. WILHELM VAUBEL (*Chem. Zeit.*, 1914, **38**, 1037—1038. Compare A., 1906, ii, 250).—Halogens may be detected by heating the organic substance with concentrated sulphuric acid in a test-tube, and holding a rod moistened with silver nitrate solution in the evolved fumes, which in the presence of a halogen will contain the corresponding hydrogen haloids. Volatile compounds are best ignited, either alone or mixed with a halogen-free, inflammable liquid, and the fumes tested as above.

For the quantitative estimation of halogens, the author maintains that in all cases, except where differentiation between the halogens is necessary, his previously described method of heating the substance with sulphuric acid gives results which are quite as trustworthy as when dichromate is used in addition, as recommended by Thies and others (A., 1914, ii, 217). With very volatile halogen compounds, moreover, the dichromate method gives no more accurate results than does Vaubel and Scheuer's method, the figures obtained in both cases being too low. G. F. M.

Action of Ammonium Bromide on Metallic Iodides. II. ICILIO GUARESCHI (*Atti. R. Accad. Sci. Torino*, 1915, **50**, 354—360. Compare this vol., ii, 167).—When heated in a long, narrow tube of hard glass with ammonium bromide, all metallic iodides, even those which, like silver iodide, withstand very high temperatures without decomposition, yield free iodine; the reactions taking place are expressed by the equations $MI+NH_4Br=MBr+NH_4I$ and $2NH_4I \longrightarrow 2NH_3+H_2+I_2$. In many, but not in all, cases the ammonium bromide may be replaced by the chloride.

By means of this reaction, as little as 0·0001 gram of potassium iodide may be detected, even when mixed with very large proportions of the chloride or bromide of an alkali or alkaline earth metal. Double iodides, such as $HgI_2,2KI$, HgI_2,CdI_2, ZnI_2,KI, give free iodine more readily when heated with ammonium bromide than when heated alone. Silver iodide gives the reaction when mixed with silver bromide, except when the latter is in very large excess. Silver chloride prevents the detection of silver iodide in the dry way, but the following procedure gives certain results, even when the iodide is present only in traces: the mixture is shaken with about ten times its weight of ammonium bromide and twenty times its weight of water, the decanted liquid being tested for iodine by either chlorine water and starch or chlorine water and chloroform.

The double iodide, $HgI_2,2AgI$, responds readily to this reaction, liberation of iodine taking place in presence of silver bromide or lead bromide, but not when silver chloride is present. With lead iodide, the reaction is not prevented by silver iodide, mercuric iodide, or lead chloride or bromide.

When a mixture of silver and ammonium bromides is heated, it fuses, boils, and yields a reddish-brown sublimate, ammonia, but not bromine, being set free. The sublimate is soluble in hot absolute alcohol, which subsequently deposits it as a red powder. This action is to be studied further. T. H. P.

Volumetric Estimation of Free Sulphurous Acid. A. SANDER (*Chem. Zeit.*, 1914, **38**, 1057—1058).—As an alternative to the iodometric estimation of free sulphurous acid, or in cases where the use of iodine would be inadmissible, titration with sodium hydroxide can be resorted to. Methyl-orange gives an end-point corresponding with the formation of sodium hydrogen sulphite, but the colour change is not very sharp. Phenolphthalein, on

the other hand, is quite useless. Although with practice the direct titration with methyl-orange will give fairly good results, a more certain end-point is obtained if the sulphurous acid is first oxidised with neutral hydrogen peroxide to sulphuric acid, which two minutes after the addition may be titrated with great accuracy in the usual way. Attempts were made to oxidise the sulphurous to sulphuric acid by boiling with mercuric chloride, but only in extremely dilute solutions could this be done without loss of sulphur dioxide. Nevertheless, it was observed that a solution of sulphurous acid, to which mercuric chloride had been added in the cold, could then be accurately titrated with sodium hydroxide, using methyl-orange as indicator, twice as much being required as was necessary for the production of $NaHSO_3$. Although the phenomenon has not yet been fully investigated, it is suggested that $NaHSO_3$ is first formed, and it then reacts with a molecule of mercuric chloride, an equivalent amount of hydrogen chloride being liberated, thus:

$$NaHSO_3 + HgCl_2 = NaSO_3 \cdot HgCl + HCl.$$

This hydrogen chloride then requires another molecule of sodium hydroxide for neutralisation. Whatever the correct explanation, the neutralised solution gives no precipitate with barium chloride, and is consequently free from sulphites. G. F. M.

Estimation of Sulphuric Acid and Potassium, especially in Potassium Salts. W. Vaubel (*Zeitsch. öffentl. Chem.*, 1914, **20**, 426—434; 1915, **21**, 1—6).—Estimation of sulphuric acid in the presence of potassium salts by precipitation with barium chloride yields untrustworthy results, and the benzidine method (A., 1902, ii, 425; 1903, ii, 691) is, therefore, recommended for the purpose. The potassium should be estimated by the cobaltinitrite process, since the perchlorate method gives unsatisfactory results when sulphates are also present. W. P. S.

Estimation of Sulphates in Flour. G. D. Elsdon (*Analyst*, 1915, **40**, 142—143).—Ten grams of the flour are warmed for one hour with 25 c.c. of concentrated hydrochloric acid, then diluted with 100 c.c. of water, filtered, and the sulphate in the filtrate precipitated by the addition of barium chloride. An ordinary flour yielded 0·012% SO_3, corresponding with 0·021% $CaSO_4$, a somewhat higher figure than those recorded by Cripps and Wright (A., 1914, ii, 816). W. P. S.

The Estimation of the Total Nitrogen in Urines, Particularly in the Presence of Sugar. Ed. Justin-Mueller (*J. Pharm. Chem.*, 1915, [vii], **11**, 171—174).—In the estimation of nitrogen in urines containing large quantities of sugar, in order to overcome the difficulty of frothing during the heating with sulphuric acid, the author advises the use of hydrogen peroxide to oxidise the sugar. If S represents the amount of sugar present in grams per litre, the amount of hydrogen peroxide (12 vols.) to be used is $S/2$ c.c., and the amount of pure sulphuric acid

$(5+S/10)$ c.c. for 10 c.c. of urine. The procedure is as follows. The 10 c.c. of urine are introduced into a 250 c.c. flask, and 5 c.c. of a 30% solution of potassium oxalate added. The calculated volume of sulphuric acid is added, and then the requisite volume of hydrogen peroxide is slowly run in. The mixture is heated so that a steady evolution of gas occurs, until the slight froth turns brown when the gas is lowered, and the rest of the procedure is as in an ordinary Kjeldahl estimation, the ammonia being finally estimated by the volumetric formaldehyde method. W. G.

The Use of Hydrochloric Acid in the Estimation of Certain Forms of Organic Nitrogen. W. A. DRUSHEL and M. M. BRANDEGEE (*Amer. J. Sci.*, 1915, [iv], **39**, 398—404).—It has been found that the nitrogen of aliphatic nitriles, cyanogen-substituted esters, amides and imides, can be estimated as ammonium chloride by heating the substance with an excess of concentrated hydrochloric acid in a sealed tube at about 200° for two to three hours. The contents of the tube are evaporated to dryness on the water-bath, and the residue heated in a drying oven at 110° for five minutes in order to remove the last traces of free hydrochloric acid. Blank experiments have shown that there is no appreciable loss of ammonium chloride under these conditions. The ammonium chloride in the residue is then titrated with standard silver nitrate solution, using potassium chromate as indicator. Small amounts of weak organic acids have no influence on the action of the indicator. In the presence of stronger acids, such as succinic acid, it is advisable to add a small quantity of sodium acetate before titration.

Experiments made with glycine show that the nitrogen in amino-compounds can also be estimated in this way, but the heating at 200° must be continued for about four hours. H. M. D.

New Ammonia Distillation Flask. GEORG WEMPE (*Zeitsch. angew. Chem.*, 1914, **27**, 624).—The flask differs from that usually employed only in that the distilling head and dropping funnel are permanently fused on to the neck, avoiding, thereby, the need for a rubber stopper. The dropping funnel is not provided with a tap, but extends to the bottom of the flask instead, so that its exit dips below the surface of the liquid throughout the distillation. G. F. M.

Estimation of Ammonia by the Boric Acid Method. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1914, **27**, 630—632).—Further experiments on the estimation of ammonia by the author's boric acid method (A., 1913, ii, 527) have shown that it will give results of considerable exactitude, provided that a considerable excess of boric acid (5—10 grams) is used to absorb the ammonia, and that efficient cooling of the distillate is provided for. The receiver should also have a narrow neck to hinder the renewal of the air above the boric acid solution. With these precautions, the amount of ammonia escaping is not greater than the equivalent of 0·05 c.c.

$N/10$-hydrochloric acid. This acid is recommended in connexion with methyl-orange or congo-red for the titration of the ammonium borate in preference to sulphuric acid, as a sharper end-point is thereby obtained. G. F. M.

Estimation of Ammonia by the Boric Acid Method. E. BERNARD (*Zeitsch. angew. Chem.*, 1914, **27**, 664).—The author has estimated the ammonia in a number of Kjeldahl analyses by Winkler's method, and has arrived at results similar to his (preceding abstract) in respect of the accuracy of the method and the precautions which it is needful to take. For 0·01—0·08 gram ammonia he recommends that 50 c.c. of 3% boric acid solution be used for the absorption, and corresponding amounts for larger quantities. G. F. M.

Analysis of Nitrites. N. BUSVOLD (*Chem. Zeit.*, 1915, **39**, 214).—A criticism of the permanganate and silver bromate methods for the estimation of nitrites. The shortcomings of Lunge's permanganate titration may be avoided by adopting Raschig's modification (A., 1906, ii, 50), titrating preferably at 50°, however, instead of in the cold, as the possibility of the loss of oxides of nitrogen is thereby minimised. The procedure is as follows: 34—35 c.c. of nitrite solution (5 grams per litre) are mixed with a slight excess (50 c.c.) of $N/10$-permanganate, to which has been added a mixture of 10 c.c. of concentrated sulphuric acid and 100 c.c. of water. After cooling, the excess of permanganate is estimated by adding potassium iodide, and titrating the liberated iodine with $N/100$-thiosulphate. The latter is standardised in the same experiment by measuring a further volume of the permanganate solution, and continuing the titration. In carrying out the silver bromate method already described (A., 1914, ii, 144), care must be taken that nitrous fumes are not evolved during the addition of the nitrite solution to the acetic acid solution of silver bromate, and that not more than 50 c.c. of dilute sulphuric acid (1 : 4) are used in the final treatment of the silver bromide precipitate, as otherwise a reduction of bromate to bromide by the sulphuric acid is possible. The author recommends 90° as the most suitable temperature at which to carry out the reduction of the silver bromate by the nitrite. G. F. M.

Colorimetric Estimation of Phosphoric Acid. E. RIEGLER (*Bull. Acad. Sci. Roumanie*, 1914, **2**, 272—275).—A colorimetric method is described for the estimation of small quantities of phosphoric acid. The method consists in precipitating the phosphoric acid as ammonium phosphomolybdate and reducing the precipitate by warming with a solution of hydrazine sulphate. In this way, a blue solution is obtained, the intensity of the colour of which is proportional to the amount of phosphoric acid present. A comparison solution is required, and this is prepared by dissolving 0·505 gram of crystallised disodium phosphate in 100 c.c. of water. One c.c. of this solution is placed in a graduated centrifuge tube,

1 c.c. of nitric acid (D 1·125) and a quantity of 30% ammonium nitrate added to fill the tube to the tenth mark, then the tube is heated and 2 c.c. of 3% ammonium molybdate solution are added, thoroughly mixed, and the solution centrifuged for two minutes. The clear solution is poured off, and the precipitate shaken with 30% ammonium nitrate solution, and again centrifuged for two minutes, and the clear solution poured off. The precipitate is then washed into a 100 c.c. flask by means of a 2% solution of hydrazine sulphate (20 c.c.), and the solution warmed. The flask is then cooled, and filled to the mark with distilled water; 1 c.c. of this solution is equivalent to 0·00001 gram P_2O_5. The solution to be analysed is treated in the same manner, and the two solutions compared in a colorimeter, and the concentration calculated. The comparison solution is stated to be quite stable and permanent.
J. F. S.

Comparative Investigation of Thomas Slag by the Methods of Lorenz, Naumann and Popp. WALTER HOLLE (*Chem. Zeit.*, 1914, **38**, 1083).—Comparative estimations of phosphoric acid in pure solutions of sodium phosphate of known strength, and in basic slags, in continuation of the experiments of Haussding (A., 1914, ii, 676). Whilst Lorenz's method gave almost ideal results with pure sodium phosphate solutions, those obtained by the methods of Popp and Naumann were, on the average, 0·48 and 0·20% higher respectively. With basic slags, Popp's method gave values averaging 0·24%, and Naumann's 0·21%, higher than Lorenz's. Popp's method is therefore to be regarded, perhaps, as equal, but certainly not superior, to Naumann's in accuracy, whilst the Lorenz method, although tedious to carry out, gives, probably, the most exact results.
G. F. M.

An Improved Method for the Estimation of Inorganic, Phosphoric Acid in Certain Tissues and Food Products. ROBERT M. CHAPIN and WILMER C. POWICK (*J. Biol. Chem.*, 1915, **20**, 461).—In their previous paper, the authors omitted to mention the previous use of picric acid for the purpose. It was employed by Greenwald (*ibid.*, 1913, **14**, 369); they regret having been ignorant of this fact.
W. D. H.

Bettendorff's Reagent [for Arsenic] and its Modifications L. VANINO and F. HARTWAGNER (*Arch. Pharm.*, 1914, **252**, 381—399).—The modification of Bettendorff's reagent recommended in the German Pharmacopœia, and also those described by Warnecke, Moberger, Winkler, Immendorffer-Kornthal, Ferraro and Carobbio, and de Jong have been compared with regard to their delicacy. The authors find that the limit of sensitivity of all the methods is the same for arsenious and arsenic acids. All the methods are suitable for the detection of quinquevalent arsenic, those of Ferraro and Carobbio and of de Jong, however, detecting only 0·03 mg. The most sensitive reagent for tervalent arsenic is de Jong's (0·0015 mg.), and for quinquevalent arsenic that of the German

Pharmacopœia (0·006 mg.). In consequence of their simple method of preparation, the comparatively still very sensitive reagents of Warnecke, Moberger, and Winkler are recommended; they detect 0·015 mg. of tervalent or of quinquevalent arsenic. C. S.

Use of the Insoluble Residue for the Estimation of Arsenic in Iron and Steel. L. Brandt (*Zeitsch. öffentl. Chem.*, 1915, **21**, 6—10).—The residue obtained when iron or steel is dissolved in dilute sulphuric acid does not contain the whole of the arsenic present in the metal. In experiments carried out by the author, the residue contained from 65 to 79% of the total quantity of arsenic, the remainder being found in the solution and in the gas evolved; in one case, the residue contained only 25% of the arsenic, whilst the solution contained 54%. When the quantities of arsenic in the residue, solution, and gases are estimated, their sum is from 3 to 9% lower than the quantity found by distillation. W. P. S.

Estimation of Arsenic, Iron, and Mercury in Sulphuric Acid. H. Nissenson (*Chem. Zeit.*, 1914, **38**, 1097).—A rapid technical method for testing commercial sulphuric acid. One hundred grams of Glover or chamber acid are heated on a sand-bath to expel nitrous fumes, then diluted with three volumes of distilled water, and slowly run through a dropping funnel, which reaches to the bottom of a litre conical flask containing 60 grams of finely granulated zinc, free from iron. Violent evolution of hydrogen must be avoided. A delivery tube leading from the flask terminates beneath the surface of a solution of bromine (1 c.c. in 100 c.c. of water acidified with a few drops of sulphuric acid). When all the sulphuric acid has been added, and the zinc is almost completely dissolved, the solution is filtered from the metallic residue, and, after washing the latter, the iron is estimated in the filtrate and washings by titration with $N/100$-permanganate. The residue is dried, mixed with freshly fused potassium hydroxide, and sublimed from a porcelain dish on to a tared gold cover, the increase in weight of which, after washing with alcohol, represents the mercury present. The arsenic which is found absorbed in the bromine solution is estimated as arsenious acid, after expelling the excess of bromine by heat and reducing the colourless solution with sodium sulphite. The estimation is carried out by titration with $N/10$-potassium bromate solution after acidifying with hydrochloric acid, using indigo as indicator. G. F. M.

The Separation of Arsenic from Tungsten. Theodor Dieckmann and Siegfried Hilpert (*Ber.*, 1914, **47**, 2444—2446).—The restrictions as to the relative proportions of arsenic and tungsten necessary to the satisfactory working of the method described earlier for the separation of arsenic from tungsten (Hilpert and Dieckmann, A., 1913, ii, 242) can be obviated by the addition of a fairly large quantity of phosphoric acid to the mixture of arsenic acid, tungstic acid, cuprous bromide (or cuprous

chloride with potassium bromide), and hydrochloric acid (D 1·16). The phosphoric acid forms a complex with the tungstic acid, so that, on distillation in a suitable apparatus, the whole of the arsenic is to be found in the distillate, and can be quantitatively titrated with iodine solution.

The estimation of arsenic in a tungsten ore is effected by fusion with sodium carbonate and sodium peroxide, extracting with water, and then, after neutralisation, distilling as described.

It is also found that arsenic can be separated quantitatively from a mixture with molybdic and vanadic acids by distillation with hydrochloric acid and a mixture of cuprous chloride and potassium bromide, and that in this case the presence of phosphoric acid is not necessary. D. F. T.

Detection and Estimation of Boric Acid in Butter. HERBERT HAWLEY (*Analyst*, 1915, **40**, 150—152).—The following process is given for the approximate estimation of boric acid in butter. Twenty grams of the sample are placed in a small beaker and heated until the fat has separated; the fatty layer is then decanted. The aqueous layer is treated with 18 c.c. of dilute hydrochloric acid (20 c.c. of concentrated hydrochloric acid diluted to 1 litre), and 10 c.c. of the mixture are transferred to a similar small beaker, cooled, and mixed with 5 c.c. of turmeric reagent (5 grams of turmeric root and 5 grams of tartaric acid extracted with hot alcohol, and the extract filtered and diluted with alcohol to 500 c.c.). The coloration which develops is compared with those yielded by definite quantities of boric acid under similar conditions. In preparing these standards, the boric acid solution is mixed with hydrochloric acid and a small quantity of milk, using 0·5 c.c. of the latter and a quantity of hydrochloric acid sufficient in each case to make the volume 10 c.c. W. P. S.

New Method for the Simultaneous Estimation of Carbon, Hydrogen, and Mercury in Organic Mercury Compounds. ARTHUR ABELMANN (*Ber.*, 1914, **47**, 2935—2938).—The process depends on amalgamating the mercury with gold. The apparatus consists of a combustion tube constricted at about 20 cm. from its forward end. It has a narrow tube fused in as near as possible to this end. Another tube, previously charged with gold leaf or gold wire and weighed, is fitted into the open end of the combustion tube, its conical end butting against the constriction, asbestos paper being employed for jointing. The constriction in the combustion tube should be placed just forward of the last burner. At the end of the operation, any products of combustion present in the annular space between the two tubes are expelled by means of a current of oxygen passed through the narrow side-tube sealed on at the end of the combustion tube. The increase in weight of the gold gives the weight of the mercury. To prepare the gold for another combustion, the mercury is volatilised by heat. It is claimed that the process is superior to that of Frankland and Duppa, because: (1) the results are as accurate as those of an

ordinary combustion; (2) the mercury can be weighed directly without drying; (3) the apparatus can be used as often as desired. A. J. W.

Apparatus for the Estimation of Carbon Dioxide by the Fresenius-Classen Method. A. SUCHIER (*Zeitsch. angew. Chem.*, 1914, **27**, 527—528).—The chief modifications in the apparatus lie in the use of sulphuric acid in a small, specially constructed washing flask for drying the carbon dioxide, and potassium hydroxide solution in a similar flask for absorbing the gas. Two guard flasks charged with concentrated potassium hydroxide solution are provided, one at each end of the apparatus, so that pure air can be drawn through by means of an aspirator. Another feature is a small double-surface spherical condenser of 6 cm. diameter connected with the gas-generating flask on the one side and with the sulphuric acid flask through a tower, charged with copper sulphate and pumice stone, on the other. All the washing flasks are constructed to prevent the possibility of back suction, and are made to stand in aluminium receptacles instead of being suspended from hooks. G. F. M.

Detection and Estimation of Small Quantities of Carbon Oxysulphide in Carbon Dioxide and Gases from Mineral Springs. L. DEDE (*Chem. Zeit.*, 1914, **38**, 1073—1075).—The formation of small quantities of hydrogen sulphide in mineral waters containing carbon dioxide is not due to the reduction of sulphates by cork or other organic matter, as suggested by Fresenius, but to the presence of carbon oxysulphide, which is slowly decomposed by the water after it has been bottled and put aside for storage. On the one hand, water containing sulphates and saturated with pure carbon dioxide did not develop in contact with pieces of cork any odour of hydrogen sulphide, whilst, on the other hand, water containing scarcely a trace of sulphate, but saturated with carbon dioxide from a mineral spring, soon became tainted with the gas. The detection and estimation of carbon oxysulphide is not possible by the ordinary methods, since in the presence of the large excess of carbon dioxide its reaction with water is extremely slow. By burning a considerable volume of the suspected gas by Dennstedt's method, however, the presence of sulphur was demonstrated, but the most certain proof was obtained by passing about 25 litres of the carbon dioxide through a warm solution of palladium chloride, collecting the precipitated palladium sulphide, freeing from metallic palladium by dissolving in hydrochloric acid and potassium chlorate, and precipitating the sulphur, then present as sulphate, by addition of barium chloride. In this way, three 25-litre portions of gas furnished 0·0057, 0·0059, and 0·0048 gram of barium sulphate respectively, corresponding with 0·0029% of carbon oxysulphide in the carbon dioxide. Similar results were obtained with carbon dioxide taken directly from the mineral spring, the water from which had developed the odour of hydrogen sulphide after bottling. G. F. M.

Estimation of Silicic Acid in Natural Waters. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1914, **27**, 511—512).—The yellow coloration generated by the addition of ammonium molybdate and hydrochloric acid to dilute solutions of silicic acid is of the same tint as a suitably diluted solution of potassium chromate, and experiments carried out with aqueous solutions of known silicic acid content, prepared from pure silicon dioxide, showed that a solution of potassium chromate containing 0·530 gram per 100 c.c. gave per c.c. the same colour intensity as 1 mg. of silicon dioxide treated as above described. The colorimetric estimation of silicic acid is, on the basis of these observations, carried out as follows. Portions of 100 and 105 c.c. of the silica containing solution or natural water are taken; to the first are added 1 gram of powdered ammonium molybdate and 5 c.c. of 10% hydrochloric acid, and to the second a quantity of the above-mentioned potassium chromate solution sufficient for the production of the same tint. The number of c.c. used for this purpose represents the number of grams of silicon dioxide in 100 c.c. of the solution. Colorimetric estimations of silica in several natural waters gave results in fair agreement with those obtained gravimetrically, and the author is of opinion that colorimetric are actually superior to gravimetric results in accuracy, owing to the numerous sources of possible error in the latter case. The presence of phosphoric acid naturally interferes with the estimation of silicic acid by the molybdate method.

G. F. M.

Estimation of Sodium and Potassium in a Mixture of their Salts. KICHIRO OKADA (*Mem. Coll. Sci. Kyoto*, 1914, **1**, 89—93).—The method depends on the slight solubility of potassium hydrogen tartrate and on the fact that when a definite quantity of a mixture of sodium and potassium salts is added to a fixed quantity of sodium hydrogen tartrate in solution, the concentration of tartrate remaining in the solution at constant volume and temperature is a function of the percentage of potassium salt in the mixture. The solution is shaken for at least five hours at 25°, and a fixed volume of the clear solution is evaporated to dryness, and the residue heated to redness. A definite volume of standard hydrochloric acid is then added, and the excess of acid estimated by means of a standard solution of sodium hydroxide.

From experiments with mixtures of varying composition, the volume of standard hydrochloric acid neutralised by the residue is determined. This volume is plotted against the percentage molar composition of the mixture, and the curve thus obtained is utilised in the evaluation of unknown mixtures. H. M. D.

Estimation of Silver in Colloidal Silver Preparations. P. W. DANCKWORTT (*Arch. Pharm.*, 1914, **252**, 497—501).—A solution of 1 gram of protargol in 10 c.c. of cold water is treated with 5 c.c. of hydrogen peroxide and 15 c.c. of 25% nitric acid, and heated under a reflux condenser for one hour. After being cooled,

the solution is diluted to 100 c.c. and titrated with $N/10$-ammonium thiocyanate, the indicator being ferric alum. The method is not suitable for collargol and other preparations containing appreciable quantities of chlorides. C. S.

Estimation of the Total Hardness of Water by Blacher's Method. HANNS FISCHER (*Zeitsch. öffentl. Chem.*, 1914, **20**, 377—381. Compare A., 1913, ii, 153, 982; 1914, ii, 670).—This method was found to be trustworthy, but it is recommended that a correction be applied when the water under examination contains appreciable quantities of iron or manganese; 10 mg. of iron or manganese are equivalent to 1° (German) of hardness.

W. P. S.

Detection and Estimation of Small Quantities of Substances in Complex Mixtures. Detection of Lead in Toxicology. G. MEILLÈRE (*Ann. Chim. anal.*, 1915, **20**, 73—77).—The principle of a method described previously (A., 1914, ii, 817) for the detection of lead (adding a quantity of a copper salt, precipitating both metals as sulphides, and then separating the lead from the copper electrolytically) may be applied to the separation of other metals. Traces of mercury may be precipitated as sulphide after the addition of copper or zinc; nickel, manganese, copper, or zinc can be precipitated together with ferric or aluminium hydroxide, fluorine with phosphates or barium sulphate, etc. The addition of copper sulphate in the detection of traces of lead in animal substances accelerates the preliminary destruction of the organic matter. W. P. S.

Electrolytic Analysis of Alloys containing Large Proportions of Lead. I. COMPAGNO (*Ann. Chim. Applicata*, 1915, **3**, 164—168).—One gram of the metal in chips is acted on with 4 c.c. of concentrated hydrochloric acid and 4 c.c. of dilute nitric acid (D 1·2) in a covered 150 c.c. beaker, and after some hours the nitrous fumes are expelled by gentle heating, and the liquid allowed to cool. The liquid is decanted, and the precipitated lead chloride washed several times by decantation with water acidified with hydrochloric acid. The total decanted liquid is rendered alkaline with sodium hydroxide solution, and treated with about 30 c.c. of sodium monosulphide (D 1·225), the lead present, and also the copper, iron, zinc, etc., present as impurities, being precipitated as sulphides, whilst the antimony and tin remain in solution. The copper sulphide is next dissolved by boiling the liquid for a few minutes with about 0·4 gram of potassium cyanide. When the sulphides have settled, the liquid is filtered, and the precipitate washed several times by decantation with hot water containing a few drops of sodium monosulphide; the filtrate is collected in a tall, 250 c.c. beaker.

The washed lead chloride is then dissolved in the minimum quantity of hot sodium hydroxide solution, and the liquid mixed with 15—20 c.c. of hot water and about 20 c.c. of the sodium

monosulphide, the precipitated sulphides being boiled with about 0·1 gram of potassium cyanide, and washed by decantation as before. The two sulphide precipitates are then filtered through the same filter, and washed with hot water containing about 30 c.c. of sodium monosulphide. The filtrate, occupying about 230 c.c., is evaporated, on a sand-bath at a gentle heat, to about 130 c.c., and is used for the electrolytic estimation of the antimony, copper, and tin (compare A., 1913, ii, 983).

The filter containing the sulphides is boiled, in the beaker in which the alloy was originally dissolved, with 25 c.c. of nitric acid (D 1·2), cold water being then added, and the insoluble filter paper and sulphur allowed to settle. The decanted liquid is filtered into a 400 c.c. beaker, and the residue treated, first with 25 c.c. of the dilute nitric acid, and afterwards with 20 c.c. of concentrated nitric acid. The liquid is boiled until the sulphur collects into yellow globules, and is then filtered, the residue on the filter paper being subjected to prolonged washing with cold water. The filtrate, of a total volume of 300—350 c.c., contains all the lead, as well as any iron, zinc, etc., and is used for the electrolytic estimation of the lead in the ordinary way, using reticulated electrodes roughened by means of a sand-blast. The residual liquid is employed for the detection, and, if necessary, estimation of impurities by the usual methods.

Parallel analyses have been made, by the above method and by that of Neumann (compare Riban, "Analyse chimique par électrol.," 263) and Nissenson (A., 1900, ii, 108), of: (1) alloys consisting almost entirely of lead, tin, and antimony; and (2) others containing appreciable proportions of other metals. The results are in excellent agreement. T. H. P.

The Volumetric Estimation of the Higher Oxides of Lead and Manganese by means of Titanium Trichloride. L. Moser (*Chem. Zeit.*, 1915, **39**, 245—247).—The author critically discusses the methods at present in use, and concludes that only the somewhat laborious distillation method of Bunsen, and Schlossberg's hydrogen peroxide method (A., 1903, ii, 184), are sufficiently trustworthy. A new procedure, using titanium trichloride as reducing agent, is described, the reaction occurring according to the following scheme:

$$PbO_2 + 2Ti^{\cdot\cdot\cdot} + 4H^{\cdot} = Pb^{\cdot\cdot} + 2Ti^{\cdot\cdot\cdot\cdot} + 2H_2O.$$

The lead peroxide, or red lead (0·2—0·4 gram), is suspended in about 100 c.c. of water, the suspension boiled, and the titanium chloride solution added in a rapid stream in an atmosphere of carbon dioxide, the flask being meanwhile well shaken. A clear solution is rapidly obtained, excess of titanium chloride manifesting itself by the violet coloration. It is essential, in order to avoid liberation of chlorine, that the titanium solution be added as quickly as possible, and it is advisable to prepare it of such strength that 1 c.c. is equivalent to 0·0035—0·005 gram of Fe. The preliminary standardisation of this solution, and the estimation of the excess present after the reduction of the lead peroxide, are

carried out by titration with ferric chloride solution, using potassium thiocyanate or methylene-blue as indicator. The results obtained in a number of estimations agreed well amongst themselves and with those obtained by Schlossberg's method. They were, on the average, slightly higher than those given by Bunsen's method. The estimation of manganese dioxide is carried out in the same way as that for lead peroxide above described, except that, on account of its less ready solubility, it is necessary to add the titanium chloride in presence of warm concentrated hydrochloric acid, and to keep the liquid gently boiling until all the manganese has passed into solution, which with natural pyrolusite may require as much as a quarter to half an hour. In the subsequent titration with ferric chloride, methylene-blue is the only admissible indicator in presence of the hydrochloric acid. "In dealing with commercial or natural specimens of either of the peroxides containing iron, it is, of course, necessary to estimate this by a subsidiary titration with titanium chloride after dissolving the sample in concentrated hydrochloric acid, and boiling off the liberated chlorine, and the value found is then to be deducted from the total amount of titanium solution required for the reduction of the peroxide in calculating the percentage of active oxygen.

G. F. M.

Detection and Estimation of Copper in Potable Water. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1914, **27**, 544).—The process previously described (A., 1913, ii, 246) for the detection of copper is found to be inapplicable in presence of ferrous iron, and the following modification is recommended. To 100 c.c. of water, ten drops of 10% Rochelle salt solution and two drops of 10% ammonia are added. The iron is thereby oxidised by the dissolved oxygen, and dissolves in the tartrate to a colourless, complex compound. The copper is then estimated colorimetrically by means of ferrocyanide, followed by potassium cyanide, as originally described, the greenish-yellow coloration being compared with that produced by a ferricyanide solution (0·1294 gram $K_3Fe(CN)_6$ in 100 c.c.; 1 c.c. = 0·25 mg. Cu) in similar circumstances.

G. F. M.

Comparison of Methods for the Estimation of Copper in Commercial Copper Sulphate (containing Iron). L. VON WISSELL and FR. KÜSPERT (*Landw. Versuchs-stat.*, 1915, **86**, 277—286).—Although trustworthy results may be obtained by precipitating the copper as sulphide from an acid solution, and subsequently converting the sulphide into oxide; by precipitating the copper by the addition of sodium thiosulphate to its acid solution, or by treating the copper sulphate solution with a slight excess of ammonia, separating the ferric hydroxide, and precipitating the copper by heating the ammoniacal solution, a more convenient and less tedious method consists in precipitating the copper as thiocyanate from a solution containing sulphurous acid. The latter method is, therefore, recommended for the estimation of copper in

the copper sulphate sold for use as an insecticide, which usually contains a quantity of iron salts. W. P. S.

New Method for the Colorimetric Estimation of Copper. G. Denigès and E. Simonot (*J. Pharm. Chim.*, 1915, [vii], **11**, 186—187; from *Bull. Soc. pharm. Bordeaux*, 1914, 337).—The method described is based on the use of a solution of hydrobromic acid prepared, when required, as follows. To 20 c.c. of a 50% solution of potassium bromide contained in a flask surrounded with ice, 10 c.c. of pure sulphuric acid are added drop by drop, taking care to avoid any heating. The clear liquid at the top is decanted off and kept in a stoppered bottle for use. For the estimation, 2 c.c. of this reagent are used, and to it are added 2 c.c. of the copper solution, to which has been added sulphuric acid until it contains 20% of it by volume. The colour is compared with that obtained by using 2 c.c. of a standard copper solution also containing 20% by volume of sulphuric acid. This method can be used for all dilute copper solutions free from iron. W. G.

Method for the Analysis of the Copper and Tin Groups. Robert Gilmour (*Chem. News*, 1915, **111**, 206—208).—The procedure recommended is briefly as follows. The metals are precipitated, as usual, with hydrogen sulphide, and the mixed sulphides are boiled with 5*N*-hydrochloric acid, which decomposes them, with the exception of mercury sulphide, copper sulphide, and arsenic sulphide; the latter is separated by extracting the residue with sodium hydroxide solution. The solution containing the remaining metals is boiled to expel hydrogen sulphide, 20 c.c. of hydrogen peroxide are added, and the mixture evaporated almost to dryness to remove excess of acid. The residue is dissolved in water, the metals are again precipitated with hydrogen sulphide, and the antimony and tin sulphides separated by extraction with sodium hydroxide solution. In separating bismuth and lead, advantage is taken of the insolubility of bismuth dichromate in sodium hydroxide solution, and the solubility of lead chromate in this reagent. W. P. S.

Analysis of Brass. Berthold Koch (*Chem. Zeit.*, 1915, **39**, 215).—When an estimation of zinc in addition to that of copper is desired, a modification of the process previously described is necessary (A., 1913, ii, 794). One gram of turnings is dissolved in a 200 c.c. beaker, covered with a watch-glass, in 15 c.c. of dilute sulphuric acid (1 : 1) and 10 c.c. of nitric acid (D 1·2). The solution is boiled until nitrous fumes cease to be evolved, and a gentle heat is continued until crystals of zinc sulphate commence to be deposited from the boiling solution. After cooling, the liquid is diluted to 150 c.c. with water, and the copper is estimated in the manner already described (*loc. cit.*). After complete deposition of the copper, the solution is cooled to 30—35°, and 18 grams of solid sodium hydroxide are added, with stirring, so that the zinc hydroxide first precipitated again dissolves. After the addition of

5 grams of potassium cyanide, the solution is heated at about 70°, and the zinc electrolytically deposited with a current of 3 amperes. Complete deposition requires about one and a-half hours, and the temperature is gradually raised to 85—95° during the operation. The time may be shortened by using stronger currents, but the author does not recommend the use of more than 5 amperes and 6 volts, and prefers the 3 amperes mentioned above. The zinc deposit adheres firmly to the electrodes, and is entirely freed from alkali by well rinsing in cold water, after which it may be dried and weighed. G. F. M.

Estimation of Manganese in Ferrovanadium. W. W. Clark (*Met. and Chem. Eng.*, 1915, **13**, 155—156; from *J. Soc. Chem. Ind.*, 1915, **34**, 357—358).—The finely powdered alloy (0·2 gram) is dissolved in a mixture of 5 c.c. of nitric acid (1 : 1) and 5 c.c. of sulphuric acid (1 : 1), with a little hydrofluoric acid if necessary. The solution is boiled, treated with 10 c.c. of silver nitrate solution (0·125%) and an excess of solid ammonium persulphate, boiled again, and cooled in cold water. After adding a few drops of saturated salt solution, the permanganic acid is titrated by means of sodium arsenite. If the alloy contains more than 5% of manganese, an aliquot portion of the original solution is taken. An estimation requires about fifteen minutes. J. C. W.

Technical Examination of Ferrovanadium. A. Heinzelmann (*Chem. Zeit.*, 1915, **39**, 285—287).—Solution of the metal is most readily obtained by treating 0·5 gram of the finely divided sample with 10 c.c. of hydrofluoric acid; when hydrogen ceases to be evolved, nitric acid is added, the solution evaporated to dryness, and the residue heated with sulphuric acid until all nitric acid has been expelled. The acid solution is then boiled with water, cooled, and diluted to 200 c.c. Fifty c.c. of this solution are now treated with a few drops of hydrogen peroxide, diluted to 250 c.c., neutralised, and heated to boiling after the addition of 50 c.c. of concentrated sulphurous acid solution. Twenty c.c. of 30% sulphuric acid are then added, a current of carbon dioxide is passed through the boiling solution for about twenty minutes in order to remove the sulphur dioxide, and the solution is titrated with $N/10$-permanganate solution; this titration gives the sum of the iron and the vanadium. The solution is then treated with a slight excess of $N/10$-ferrous ammonium sulphate solution (spot tests with potassium ferricyanide being used as the indicator), the excess of ferrous salt is titrated with $N/10$-permanganate solution, and the titration with the latter solution continued until the mixture exhibits a reddish-brown coloration; the number of c.c. of $N/10$-permanganate solution used in the last titration is multiplied by 0·00512 to obtain the quantity of vanadium, and the iron is found by difference. W. P. S.

The Analytical Investigation of Tungsten. II. Hans Arnold (*Zeitsch. anorg. Chem.*, 1914, **88**, 333—340. Compare A., 1914, ii, 679).—Silicon is usually present in tungsten as oxide, and is

best estimated by heating the tungstic acid with hydrofluoric acid. A deep platinum crucible must be used, or particles of tungstic oxide are lost; or an alkaline solution of the tungsten may be prepared, mixed with tartaric acid and acidified with formic or acetic acid. The solution is evaporated to dryness in a platinum dish, dried at 120°, and extracted with hot water. Silica remains insoluble, and is ignited and then heated with hydrofluoric acid.

The estimation of arsenic is rendered difficult by the formation of arsenotungstates. Phosphorus and arsenic may both be estimated by dissolving about 10 grams of tungstic acid in 100 c.c. of 20% sodium hydroxide, and boiling thirty minutes. The arsenic is then precipitated with magnesia mixture, and allowed to remain for twelve hours. The precipitate is distilled with hydrochloric acid and cuprous chloride. For phosphorus, the magnesia precipitate is evaporated with hydrobromic acid to remove arsenic, and phosphorus is then estimated by means of molybdate.

Sulphur is precipitated as barium sulphate from concentrated solution, adding a little oxalic acid. The precipitate must be washed with hydrochloric acid and alkali hydroxide after ignition. With finely divided tungsten, sulphur is best estimated by dry combustion, collecting the sulphur dioxide in sodium hydroxide and bromine.

Carbon, when the metal is in fine powder, is also estimated by combustion. Massive metal must be dissolved electrolytically, using a low current density and avoiding the evolution of gas at the anode. The anode residue is collected on asbestos, dried, and submitted to combustion. C. H. D.

[Estimation of Tungsten.] V. K. Kantschev (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 729—742).—See this vol., ii, 349.

Simple Method of Estimating the Antimony in Stibnite. F. Lehmann and B. Lokau (*Arch. Pharm.*, 1914, **252**, 408—412).—About 0·2 gram of the finely powdered mineral is boiled for two minutes with 5 c.c. of officinal sodium hydroxide and 10 c.c. of water. After dilution with 10 c.c. of water, the liquid is filtered into a 200 c.c. glass-stoppered, Erlenmeyer flask, the residue being washed twice with 10 c.c. of hot water. The combined filtrate and washings are boiled during about fifteen minutes with 25 c.c. of officinal hydrogen peroxide, treated with 25 c.c. of 25% hydrochloric acid, and cooled, 1—2 grams of potassium iodide are added, and the solution is diluted with 25 c.c. of water, and titrated after five minutes with $N/10$-sodium thiosulphate. Towards the end of the titration, the mixture must be shaken vigorously after each addition of the thiosulphate. C. S.

Secondary Colorations in Iodometric Titrations. A. Kolp (*Chem. Zeit.*, 1915, **39**, 299—300).—In the iodometric titration of antimony pentachloride, an indistinct end-point is obtained when the solution contains an insufficient quantity of hydrochloric acid (compare A., 1908, ii, 599), whilst the continued liberation of

iodine after the titration is completed is due to the presence of atmospheric oxygen in the hydrochloric acid used. The latter should be treated previously with a current of carbon dioxide.

W. P. S.

Separation of Ethane and Ethylene by Fractional Distillation in a Vacuum at Low Temperatures. G. A. Burrell and I. W. Robertson (*J. Amer. Chem. Soc.*, 1915, **37**, 896—902).—The method of separating gases by fractional distillation in a vacuum (A., 1914, ii, 741; this vol., ii, 100) has now been applied to a mixture of equal volumes of ethane and ethylene, the b. p.'s of which differ by only 10°. The object of this investigation was to test the method and determine the amount of work involved in the separation of such a mixture.

The results showed that the separation can be almost completely effected, but that the work involved is exceedingly tedious in comparison with that required for the separation of gases with widely separated b. p.'s. As is invariably the case with liquids that tend to separate into two components, the less volatile component (the ethane) was more easily obtained in a pure state than the other.

E. G.

Variation with Temperature of the Refractive Index of Essential Oils. Karl Irk (*Pharm. Zentr.-h.*, 1914, **55**, 789—793).—The accuracy with which the index of refraction can be measured renders it of value as a characteristic of an essential oil, although the range of indices is so narrow. The alteration of n_D for 1° was given by Harvey and Wilkie (*Chemist and Druggist*, 1910, **76**, 442) as 0·00046, and by Schimmel & Co. as 0·00035. The author has now examined fifty-three oils, and finds the value, from 10—30°, 0·00038 to 0·00052, or, as a mean, 0·00044. J. C. W.

The Variation with Temperature of the Density of Essential Oils. Karl Irk (*Pharm. Zentr.-h.*, 1914, **55**, 831—837).—The author discusses the value of the density of an essential oil as a characteristic, and, in view of the varying standards to which this constant is referred, has determined the influence of temperature in the case of nearly fifty oils. The mean alteration for 1° is found to be: between D_4^{15} vac. and D_4^{20} vac., 0·00076; between D_{15}^{15} and D_{15}^{20}, 0·000746; and between D_{15}^{15} and D_{20}^{20}, 0·000598. These values supplement similar data of Schreiner and Downer, Schimmel & Co., and others. J. C. W.

Estimation of Methoxyl in Beechwood Tar. J. Sureda Blanes and Adolfo Gonsález (*Anal. Fis. Quim.*, 1915, **13**, 158—160).—A description of a method for valuing the creosotes of beechwood by estimating the guaiacol present by the Zeisel method. A. J. W.

The Cause and Significance of an Abnormal Reaction Obtained in Testing Urine for Sugar with Fehling's Solution. W. Cramer (*Biochem. J.*, 1915, **9**, 71—77).—A reduction of cupric

salts to metallic copper can be brought about by concentrated aqueous solutions of the reducing sugars. It takes place readily in urine when the other urinary constituents are present in normal concentration, and is facilitated by the fact that certain constituents hold cuprous oxide in solution. When the reaction occurs, it indicates marked glycosuria without polyuria, and not typical diabetes mellitus. W. D. H.

A New Test for Reducing Sugars in the Urine. WILLIAM CRAMER (*Biochem J.*, 1915, **9**, 156—160).—The test depends on the reduction of mercuric oxide to metallic mercury in a feebly alkaline solution; the degree of alkalinity is important, and full directions are given for the preparation of the reagent. It is more sensitive than Fehling's or Nylander's tests, and is free from certain objections to which both of these tests are open. W. D. H.

The Use of Colloidal Iron in the Estimation of Lactose in Milk. REUBEN L. HILL (*J. Biol. Chem.*, 1915, **20**, 175—177).—Ten grams of milk are diluted with about 25 c.c. of a 10% solution of dialysed ferric hydroxide, and filtered. The filtrate is clear and free from protein; in it the lactose is estimated by Benedict's method. W. D. H.

Pyridine as Solvent in the Estimation of Active Hydrogen in Organic Compounds by means of Magnesium Methyl Iodide. V. TH. ZEREWITINOV (*Ber.*, 1914, **47**, 2417—2423. Compare A., 1912, i, 841; 1911, i, 101; 1908, i, 593; 1907, ii, 509).—In reply to the adverse criticism of Tanberg (A., 1914, ii, 222), the author maintains that, with carefully dehydrated pyridine (A., 1907, ii, 509) as a solvent, groups containing active hydrogen can be trustworthily estimated with magnesium methyl iodide.

The formation of gas from pyridine and magnesium methyl iodide in the apparent absence of any third compound, as observed by Tanberg, may have been due to the presence of excess of methyl iodide, which would give rise to methyl pyridinium iodide; this is able to react with magnesium methyl iodide, producing ethane; on the other hand, the evolution of gas may have been due to incomplete drying of the liquid, or also to possible chemical change, such as oxidation or reduction in the pyridine induced by the excessively prolonged digestion with barium oxide. That any one of these causes may produce an effect similar to that described by Tanberg is demonstrated by experimental results. D. F. T.

Formation of Hydrogen Cyanide in the Germination of Seeds. III. CIRO RAVENNA (*Atti R Accad. Lincei.*, 1914, [v], **23**, ii, 222—226; Compare Ravenna and Zamorani, A., 1910, ii, 1099; Ravenna and Vecchi, A., 1912, ii, 194).—The paper deals chiefly with the estimation of hydrogen cyanide in vegetable products. The method recommended by the author is to collect the distillate in magnesia water, and titrate with silver nitrate in the presence of chromate. R. V. S.

A Colorimetric Method for the Estimation of Amino-acid α-Nitrogen. VICTOR JOHN HARDING and REGINALD M. MACLEAN (*J. Biol. Chem.*, 1915, **20**, 217—230).—The method is one in which the intensity of the blue colour is estimated which is produced by triketohydrindene hydrate and pyridine. Its accuracy is equal to that of Van Slyke's method; but it is not accurate for cystine. The method is applicable to the estimation of the amino-acid α-nitrogen set free in protein hydrolysis. W. D. H.

Possibility of Titrating the Monosubstituted Amino-group of Amino acids by the Formaldehyde Method. ANTONINO CLEMENTI (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 352—359).—Experiments with sarcosine show that, even when mono-substituted, the amino-group of amino-acids reacts with formaldehyde in accordance with the equation:

$$2R{\cdot}NHR' + CH_2O = NRR'{\cdot}CH_2{\cdot}NRR' + H_2O.$$

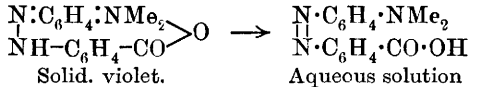
When titrated in presence of formaldehyde according to Sörensen's method (A., 1908, i, 115), these mono-substituted amino-acids behave as monobasic acids; the titration must be continued until the phenolphthalein exhibits an intense red colour. T. H. P.

Detection of Cinnamic Acid. D. SCHENK and H. BURMEISTER (*Pharm. Zeit.*, 1915, **60**, 213—214).—The test recommended depends on the oxidation of the cinnamic acid to benzaldehyde, and the identification of this by its odour and by its reaction with phenol and sulphuric acid. The substance to be tested is acidified with phosphoric acid and extracted with ether; the ethereal solution is then shaken with sodium carbonate solution, the aqueous layer is separated, extracted twice with ether (this is essential, particularly in the case of fruit juices, in order to remove small quantities of furfuraldehyde compounds), and very dilute potassium permanganate solution is added, drop by drop, until the pink colour is only just discharged. The solution is now extracted with ether, the ethereal solution is treated with 10 drops of an ethereal 5% phenol solution, allowed to evaporate at the ordinary temperature, and a few drops of concentrated sulphuric acid are added to the residue. A yellow coloration is obtained, even when the quantity of benzaldehyde formed from the cinnamic acid is too small to be identified by its odour. The furfuraldehyde compounds which may be present give, if not removed completely, a faint orange coloration, which cannot be mistaken for that yielded by benzaldehyde. Benzoic acid, if present in addition to cinnamic acid, may be detected by a test described by Fleury (A., 1914, ii, 78). W. P. S.

A New Colour Reaction for Salicylic Acid. P. A. W. SELF (*Pharm. J.*, 1915, **94**, 521).—The substance to be tested is moistened with a cold mixture of equal volumes of 40% formaldehyde and concentrated sulphuric acid, and then stirred with a little ammonium vanadate. The quantities of the reagents should be adjusted to the amount of the substance; 1 mg. of salicylic acid

should have about two drops of the liquid and 2—3 mg. of the vanadate. Salicylic acid gives no colour until the ammonium vanadate is added, when an immediate Prussian-blue colour, changing rapidly to greenish-blue and then green, is the result. The test responds with 0·02 mg. of the acid, and is very pronounced with 1 mg. It is only given by salicylaldehyde and methyl salicylate, the difference in the colours (chocolate) caused by phenol being particularly distinct. J. C. W.

Acidimetric Estimation of Picric Acid and the Interatomic Change of the Indicator Methyl-Red. St. Minovici and C. Kollo (*Bull. Acad. Sci. Roumanie*, 1914–15, **3**, 61—71).—It is shown that when picric acid is titrated with alkali, using either lacmoid or phenolphthalein as indicator, an excess of alkali above that theoretically necessary is required to bring about the colour change. If, however, methyl-red, *p*-dimethylaminoazobenzene-*o*-carboxylic acid, is used, the colour change is sharp, and the amount of alkali required to effect the change agrees absolutely with the amount required theoretically. The reason for the inaccuracy in the former case is that before the solution changes from yellow to red, it passes through a series of brown tints, whilst in the case of methyl-red the colour change is from red-violet to colourless, and consequently the yellow solution of picric acid changes from the red-violet colour sharply to its original yellow colour. The colour change of methyl-red has been examined by means of measurements of its absorption spectrum in aqueous alcohol solution, and also in the presence of sodium hydroxide and hydrochloric acid. The results are of a similar nature to those found by Hantzsch for helianthin (A., 1908, i, 469), the change being represented by



Solid. violet. Aqueous solution yellow.

J. F. S.

Analyses of Milk. Estimation of the Dry Residue and of the Total Nitrogen. G. Meillère (*J. Pharm. Chim.*, 1915, [vii], **11**, 167—170).—For the estimation of total solids, the author advises the evaporation of 5—10 c.c. of the milk in a flat glass dish 7 cm. in diameter at 37° in an incubator. The time required is three to four days, and the residue obtained is quite white, and contains the lactose in its hydrated form. For the estimation of total nitrogen, he advises that the milk (10 or 20 c.c.) should be evaporated to dryness on a water-bath prior to its treatment with sulphuric acid by the Kjeldahl method. One or two details of minor importance are mentioned in connexion with the final distillation. W. G.

Estimation of Formaldehyde and Hexamethylenetetramine. Formalin Pastilles. W. Stüwe (*Arch. Pharm.*, 1914, **252**, 430—435).—Formaldehyde is accurately estimated by the follow-

ing method. A solution of 1·0 gram of mercuric chloride in 20 grams of water is shaken with 0·5 gram of gum arabic and 3·0 grams of potassium iodide, and 10 c.c. of 15% sodium hydroxide are added to the clear solution. Ten c.c. of the reagent are added to 1 c.c. of the formaldehyde solution in 100 c.c. of water, and, after one minute, the mixture is acidified with 20 c.c. of dilute acetic acid, external cooling being employed if necessary. The liberated mercury is dissolved in 25 c.c. of $N/10$-iodine (1 c.c. = 0·0015 gram of formaldehyde), and the excess of the latter is titrated with $N/10$-thiosulphate.

Hexamethylenetetramine is estimated by heating on the water-bath for fifteen minutes a 250 c.c. flask fitted with a reflux condenser, and containing 0·5 gram of hexamethylenetetramine, 100 c.c. of water, and 10 c.c. of 25% hydrochloric acid. The flask is then cooled, the condenser is rinsed and removed, and the flask is filled to the mark. The formaldehyde in 10 c.c. of the solution is estimated by the preceding method.

The formalin pastilles used for disinfecting purposes contain trioxymethylene, the amount of which (as formaldehyde) is estimated by adding 0·025—0·03 gram of the powdered pastille to the Nessler's reagent, prepared as described above; 20 c.c. of $N/10$-iodine suffice to dissolve the liberated mercury. The pastilles contain 99·48% of formaldehyde. C. S.

Method for the Separation and Identification of Certain Homologous α-Diketones. J. M. Johlin (*J. Amer. Chem. Soc.*, 1915, **37**, 892—896).—The author has observed that pyroligneous acid contains considerable quantities of diacetyl, and that the latter can be precipitated as the nickel salt of dimethylglyoxime by the addition of solutions of nickel chloride, hydroxylamine hydrochloride, and ammonia. On applying this method to the estimation of diacetyl in pyroligneous acid, it was found that other ketones, homologous with diacetyl, were present, and it was therefore necessary to devise a qualitative scheme for their separation and identification.

A method has been worked out for the separation of methylglyoxal, diacetyl, and methyl ethyl diketone. The nickel salts of the dioximes are precipitated, and extracted with ether; the salt of methylethylglyoxime is dissolved, together with traces of that of methylglyoxime. The residue is extracted with dilute ammonia, which dissolves the methylglyoxime salt and traces of the dimethylglyoxime salt. The full scheme is given in a diagrammatic form, showing the various steps to be taken to isolate the pure dioximes from a mixture containing minute quantities of their insoluble nickel salts. The dioximes are identified by their m. p.'s. E. G.

Qualitative Separation and Identification of Some Hydroxymethylanthraquinones. E. Monroe Bailey (*Amer. J. Pharm.*, 1915, **87**, 145—154).—The common cathartic drugs, senna, rhubarb, aloes, and various species of buckthorn, contain a group of colour principles—the hydroxymethylanthraquinones. Although

the author has not been able to find a reaction which would serve to distinguish these drugs from each other, the separated hydroxymethylanthraquinones present differences towards certain reagents, these differences being particularly marked in the cases of chrysophanic acid (1 : 8-dihydroxy-3-methylanthraquinone) and emodin (trihydroxy-2-methyl-9 : 10-anthraquinone). To obtain the mixed colour principles, the fluid extract of the drug is diluted with water, treated with an excess of normal lead acetate, the lead precipitate decomposed with sulphuric acid, and the solution extracted with benzene. The benzene solution is then extracted successively with ammonium carbonate, sodium carbonate, and sodium hydroxide solutions, by which means unidentified anthraquinone derivatives, emodin, and chrysophanic acid are extracted in the order named. The aqueous extracts are acidified separately, extracted with ether, and the residues obtained from the ethereal solutions examined as to their melting points and colour reactions. Chrysophanic acid, as separated from various drugs, is not pure, and has m. p. varying from 162° to 191°, whilst emodin has m. p. about 250°; aloes emodin, however, has m. p. 216°. The most distinctive colour reaction is obtained with sulphuric acid. Emodin yields an intense pink coloration, which is not altered by dilution with water; the emodin derived from aloes is an exception, giving a red-brownish coloration, changing to yellow on dilution. Chrysophanic acid gives a reddish-orange coloration, and, on dilution, a yellow solution and a yellow precipitate. The substance extracted by ammonium carbonate solution from the benzene extract yields a violet coloration with sulphuric acid.

W. P. S.

Examination of Officinal Copaiba Balsam. Ernst Deussen (*Arch. Pharm.*, 1914, **252**, 590—600).—Turner's colour reaction, as described in the German Pharmacopœia for the detection of gurjun balsam in copaiba balsam, gives quite misleading information. The author has examined twelve samples of Maracaibo balsam. According to Turner's test, two of them were adulterated and one was suspect. Optical examination, however, showed that none of them was pure. The author's method of examining copaiba balsams is as follows. The solubility in chloroform and in absolute alcohol, the density, and the amount of the residue after distillation at 100°, give useful information, but the most searching test is an optical one. The balsam is distilled with steam almost as completely as possible, the oil in the distillate is dried with sodium sulphate and filtered, and its rotation is determined. The values of α, calculated for a 10-cm. tube, must lie between $-2{\cdot}5$ and $-14°$ if the original balsam was unadulterated; balsams, the oils from which are more or less dextrorotatory, are certainly adulterated.

Adulterated balsams which fail to respond to Turner's reaction may give positive results if the oils are separated and fractionally distilled; one or other of the fractions will respond to Turner's test, as modified by Deussen and Eger (A., 1912, ii, 812). C. S.

Plant Micro-Chemistry. V. Calumba Root. O. TUNMANN (*Pharm. Zentr.-h.*, 1914, **55**, 775—780).—Many solvents and reactions of calumbin, the bitter principle of Calumba root, are described, as well as the appearance of the perfect crystals obtained on a slide from hot glycerol. Calumbin also crystallises readily from ethyl acetate, and can be extracted from the dried drug and identified quite speedily under the microscope with the help of this solvent. It is also shown how easily the Calumba alkaloids can be detected by the formation of the iodide and hydrochloride crystals from a few micro-sections of the root. J. C. W.

Critical Examination of the Most Important Methods for the Estimation of Prussian Blue in the Cyanide Mud from the Bueb Cyanide Washer and in the Gas Purifiers. G. ANDERSON (*Zeitsch. angew. Chem.*, 1914, **27**, 532—535).—Bueb's method, which consists in boiling the cyanide mud with aqueous potassium hydroxide, and, after filtering, titrating the acidified filtrate with a standard zinc sulphate solution, using ferric chloride as external indicator, suffers from the disadvantage of the uncertainty in the end-point. Errors, due to different quantities of sulphuric acid being added before titration, and to the concentration of the ferrocyanide solution, are, naturally, avoidable by adhering strictly to the specified quantities, both in standardising the zinc sulphate solution and in the subsequent titration of the filtrate from the mud.

Drehschmidt's method (A., 1893, ii, 50) gives somewhat varying results, in addition to requiring a number of expensive reagents of considerable purity, and is therefore not recommended. In carrying out the estimation, it is necessary to continue the boiling with ammonium sulphate and mercuric oxide for thirty minutes, and to ensure that all reagents are free from chlorine. If sulphur is present, there is also a danger of the formation of thiocyanate, and cyanide thus combined escapes estimation.

In the Feld-Witzeck method (compare A., 1904, ii, 214), the decomposition of the mercuric cyanide is not complete unless a considerable excess of soluble chloride is added, and both liquids must be boiling when the mercuric chloride is added. With these precautions, this method is regarded as the most trustworthy, and the following slightly modified procedure is recommended: 20 grams of cyanide mud are diluted to 100 c.c., and 10 c.c. mixed with 1 c.c. of N-ferrous sulphate solution and 5 c.c. of $8N$-sodium hydroxide in a glass mortar. Fifty c.c. of $3N$-magnesium chloride are added after five minutes, and the whole washed into a distilling flask. After boiling ten minutes, 100 c.c. of boiling $N/10$-mercuric chloride solution are added, followed, after a further ten minutes' boiling, by 30 c.c. of $4N$-sulphuric acid. The liquid is then distilled for twenty to thirty minutes, the hydrogen cyanide being collected in 20 c.c. of $2N$-sodium hydroxide, and titrated with silver nitrate. G. F. M.

The Urease of the Soja Bean and its Application to the Quantitative Estimation of Urea. FRITZ EIGENBERGER (*Zeitsch. physiol. Chem.*, 1915, **93**, 370—377).—The author recommends

Marshall's method for the estimation of carbamide as modified by van Slyke (A., 1914, ii, 822). R. V. S.

Estimation of Certain Opium Alkaloids by Decomposition of their Methoxyl Groups. J. GSELL and B. MARSCHALKÓ (*Zeitsch. anal. Chem.*, 1914, **53**, 673—678).—Zeisel's method for the estimation of methoxyl groups may be applied to the estimation of codeine, thebaine, papaverine, narcotine, and narceine. One gram of codeine yields 0·774 gram of silver iodide; 1 gram of thebaine, 1·90 grams; 1 gram of narcotine, 2·266 grams; 1 gram of narceine, 2·110 grams; and 1 gram of papaverine, 3·187 grams. Narcotine and narceine contain, apparently, four methoxyl groups, and not three. W. P. S.

Possible Source of Error in Some Alkaloidal Assays. P. A. W. SELF (*Pharm. J.*, 1915, **94**, 585—586).—When alkaloids are liberated by ammonia from an aqueous solution of their salts, and then extracted with ether, it is essential to wash the ethereal solution with water in order to remove any trace of ammonium salts, since, on evaporation of the ethereal solution, reaction takes place between the alkaloid and any remaining ammonium salt, with loss of ammonia and formation of an alkaloidal salt. Titration of the residue, therefore, tends to give low results. W. P. S.

Measurement of the Ferment Action of Yeast by means of the Liquid Interferometer. OTTOMAR WOLFF (*Chem. Zeit.*, 1915, **39**, 197—198).—The activity of yeast can be measured by the interferometer in exactly the same way as that of diastase (this vol., ii, 296), and with even greater exactitude, since the refractive indices of sugar and alcohol solutions of the same strength show a considerable difference, being for 9·95% solutions 1·34612 and 1·33839 respectively. The method of procedure was similar to that already described, 1 cm. chambers being used in the interferometer, and a suspension of 10 grams of the yeast under investigation in 200 c.c. of water was treated with 10 c.c. of 10% sugar solution. One portion was heated at 60° to kill the ferment, and was then used as the blank, and another portion placed in a thermostat at 28·5° was examined hourly. The liquids were clarified by centrifugation before placing in the interferometer chambers. For reasons which still require explanation, considerable irregularities were observed during the first hour or so of the fermentation, but after this the action was quite uniform, and a comparison of the activity of various kinds of yeasts could then be accurately accomplished. G. F. M.

The Hopkins-Cole Reaction for Protein. H. G. D. BREIDAHL (*Biochem. J.*, 1915, **9**, 36—37).—The sulphuric acid used is a factor in the success of the reaction; the addition of various reducing agents to improve the acid for this purpose was tried, but the most satisfactory is granulated zinc. W. D. H.

An Improved Hæmin Test for Blood. WILLIAM BEAM and GILBERT ARTHUR FREAK (*Biochem. J.*, 1915, **9**, 161—170).—Acetic is

the best acid to employ; not more than 0·01% of sodium chloride is advisable, and for unwashed blood-stains even that is not necessary. There is no advantage in substituting other salts. In performing the test, evaporation should be slow, and, provided this and other precautions given are followed, the test is very sensitive, even with blood-stains years' old, and to blood heated at 110° or mixed with earth, or rusty iron. W. D. H.

Surface Tension and the Examination of Medicines. P. W. DANCKWORTT (*Arch. Pharm.*, 1914, **252**, 502—513).—The author applies Traube's stalagmometric method of measuring surface tension to the examination of several important, but not very highly active, drugs, such as valerian, rhubarb, black alder, etc., for the examination of which, and of medicinal preparations obtained from them, there is no method available. By determining the change in the drop-number of solutions of night-blue and of wool-violet-S produced by the addition of these substances, information can be obtained as to the presence of certain anions, cations, and other substances.

The paper is only of a provisional character. C. S.

Chemical Analysis of Soils. ALEXIUS A. J. VON 'SIGMOND (*Bied. Zentr.*, 1915, **44**, 76—78; from *Intern. Mitt. Bodenk.*, 1914, **4**, 336).—From the results of analyses by different methods for ascertaining the maximum solubility of soil constituents, the conclusion is drawn that it is desirable to employ Hilgard's method of extracting soils with hydrochloric acid (D 1·115) on a boiling water-bath for one hundred and twenty hours. By this method, in which 100 c.c. of acid are used with 10 grams of air-dried soil, greater amounts of nearly all the constituents are dissolved than by the official American method, by boiling for one hour with acid of the same strength as that employed by Hilgard, and by the Russian method of heating for ten hours on a water-bath with 10% hydrochloric acid. N. H. J. M.

Chemical Analysis of Soils. E. A. MITSCHERLICH (*Bied. Zentr.*, 1915, **44**, 74—76; from *Intern. Mitt. Bodenk.*, 1914, **4**, 321).—In extracting soils with acid of a given strength the amount of active agent is not the same at the end as at the beginning, and will be quite different with different soils. It would, therefore, be preferable to make the acidity of a constant strength at the end of the extraction, instead of at the beginning, by adding during the extraction so much acid as is used up. The continuous-extraction method has the advantage that the dissolved salts, being removed, do not interfere.

As regards a method which will give results in accordance with vegetation experiments, it is considered impossible to devise such a method until the necessary vegetable-physiological foundations have been made. At present these do not exist. N. H. J. M.

General and Physical Chemistry.

The Principal Series in the Spectra of the Alkali Metals. W. Marshall Watts (*Phil. Mag.*, 1915, [vi], **29**, 775—783).—It is shown that the frequency ν of the principal series lines in the spectra of the alkali metals can be satisfactorily represented by the formula $\nu = \nu_0 - 109675/(m+\mu+c/(m-1))^2$, in which ν_0 is the convergence frequency of the series, μ and c are constants, and m represents the successive integral numbers, beginning with $m=2$.

H. M. D.

Optical Investigation of the Constitution of Inorganic Salts, Acids and Esters. Konrad Schaefer [with H. Niggemann and W. Köhler] (*Zeitsch. Elektrochem.*, 1915, **21**, 181—191).—A study of the absorption spectra of sulphur dioxide, sulphurous acid and its salts and esters, hypochlorous acid and its salts and esters, chlorine dioxide, chlorous acid and the chlorites, and nitric acid, nitrates and alkyl nitrates, has been made over a large range of concentration and variation of experimental conditions. The measurements were made photographically by the Hartley-Baly method, and the results plotted as curves, the ordinates of which are the logarithms of the thicknesses of the layers, and the abscissæ the vibration numbers (frequencies). Gaseous sulphur dioxide, at pressures of 60—3 mm., possesses a strong absorption band, which persists when the gas is dissolved in water, although a little broadened in the direction of the ultra-violet; the maximum is also moved in the same direction. When these spectra are compared with that of sodium sulphite, which is of a different nature, it is seen that the equilibrium in the reaction $SO_2 + H_2O \rightleftarrows H_2SO_3$ lies strongly to the left of the equation. On neutralising a solution of sulphur dioxide with sodium hydroxide, the absorption spectrum changes from a selective absorption to a total absorption in the ultra-violet. This is little affected by an excess of sodium hydroxide, which indicates that sodium sulphite and its ions have the same absorptive properties. Sodium hydrogen sulphite shows a weak absorption spectrum of the same nature as that of sulphurous acid. In the latter case, the hydrogen sulphite was obtained by adding the theoretical quantity of sodium hydroxide to the acid, but if it is prepared by adding the correct quantity of sulphuric acid to the normal sulphite, an entirely different absorption spectrum is obtained, which in twenty-four hours had changed to the spectrum obtained by the other method of preparation. A solution of potassium pyrosulphite ($K_2S_2O_5$), when freshly prepared, gave a stronger absorption than the hydrogen sulphite, but in forty-eight hours the spectrum had become that of the latter. Further measurements were made with sulphurous acid in the presence of sulphuric acid, and also with solutions of $SO_2(OEt)\cdot Et$ and $SO(OEt)_2$. A discussion of the possible significance of the changes in the absorption spectra is entered into.

The absorption spectra of hypochlorous acid in water and in light petroleum solutions are similar, consisting of a broad band in the ultra-violet, which is somewhat weaker in the latter case. The ethyl ester shows a similar spectrum in both solvents, so that the same constitution is to be applied to hypochlorous acid and its ethyl ester. When hypochlorous acid is exactly neutralised by sodium hydroxide, a new absorption spectrum makes its appearance with a broad, deep band, which is further deepened when the hydrolysis is driven back by an excess of sodium hydroxide, whilst the persistence of the band is increased. The lithium, barium, and potassium salts yield similar spectra, so that a different constitution is in all probability to be applied to the hypochlorites from that adopted for the acid and esters.

Gaseous chlorine dioxide has an absorption spectrum consisting of numerous small bands, which reach into the visible region. When dissolved in light petroleum, the spectrum of chlorine dioxide is less sharp and a trifle displaced. When dissolved in water, the spectrum is practically that of gaseous chlorine dioxide, except that some of the narrow bands have joined up, and as chloric acid is non-absorbent, it follows that chlorine dioxide exists as such when dissolved in water. The chlorites are non-absorbent.

The absorption spectrum of nitric acid has been measured for concentrations from 0·05—23·7*N*. It is shown that at the lower concentrations Beer's law holds up to about 1*N*-solutions. With concentrations above this value, a gradual displacement toward shorter wave-lengths occurs, and at the same time a decrease in the persistence takes place, until eventually the band has disappeared. The methyl and ethyl esters behave like the concentrated acid, both in the pure condition as liquid or vapour, and also in solution in various solvents. The alkali and alkaline earth nitrates are like the dilute nitric acid solutions. It appears, therefore, that the NO_3 group has two constitutions: (1) a form which yields selective absorption, which occurs in dilute solutions of nitric acid, in the nitrates of strongly electropositive metals, and in the nitrate ion; and (2) a form with the end absorption, which occurs in concentrated nitric acid and in the esters. The paper concludes with a discussion of the connexion between electrolytic dissociation and variability of absorption spectra. J. F. S.

The Form of Ultramicroscopic Silver Particles. R. GANS (*Ann. Physik*, 1915, [iv], **47**, 270—284. Compare A., 1912, ii, 508).—The absorption curve for colloidal silver solutions has been calculated on the assumption that the particles have the same refractive index and absorption coefficient as metallic silver, and that the particles may be considered to have the form of ellipsoids of revolution. The calculation indicates a maximum of absorption at $\lambda = 394\ \mu\mu$ if the particles are spherical. If ellipsoidal, there are two maxima, the distance between which increases with increasing eccentricity.

A solution of colloidal silver, prepared from "collargol," after

being subjected to ultra-filtration, was found to exhibit maximum absorption at $\lambda = 412\,\mu\mu$. This is considered to indicate that the ultramicroscopic particles are approximately spherical in shape. The discrepancy between the calculated and observed values of the absorption maximum is attributed to the presence in the solution of a small proportion of particles of larger size. This interpretation is in agreement with the theoretical deduction that for spherical particles the absorption maximum shifts towards the visible spectrum as the diameter increases. H. M. D.

The Absorption Spectra of the Dioximines. I. L. A. Tschugaev and A. Glebko (*Zeitsch. anorg. Chem.*, 1914, **89**, 241—256).—The metallic dioximines $M(D_2H_2)$, where

$$D = \begin{pmatrix} R\cdot C{:}NO \\ R\cdot \dot{C}{:}NO \end{pmatrix}$$

(A., 1906, i, 814), are highly coloured. Their absorption spectra have now been examined by means of a quartz spectrograph. The dioximines of nickel, cobalt, palladium, and platinum exhibit absorption in the visible and ultra-violet region, the characteristic band having its maximum between $1/\lambda\,3500$ and 4000. The α-dioximes themselves have only continuous absorption.

Of the compounds of methyl*iso*butylglyoxime, the nickel and platinum derivatives give distinct absorption bands, the latter being displaced towards the red. The palladium curve is intermediate in position, but only presents a step in place of a band. The molecular weight of the dioxime has little influence on the absorption.

When the simple dioximines $M(D_2H_2)$ are compared with those of co-ordination number 6, the absorption bands of the latter are found to be displaced towards the red. The compound $PtDH_2Cl_2$, obtained by the action of concentrated hydrochloric acid on platinum methylethylglyoximine, has a greatly lowered absorption, whilst the band is displaced towards the ultra-violet.

The compounds of tervalent cobalt give a characteristic band, nearer to the ultra-violet. The complex cation $[Co(NH_3)_2D_2H_2]$ has a characteristic band at 4050, which is independent of the nature of the anion, but when the negative group enters the inner co-ordination sphere, as in $[CoClNH_3\cdot D_2H_2]$ and $[CoNO_2\cdot NH_3\cdot D_2H_2]$, the spectrum is altered, the former having no absorption band. The replacement of NH_3 by NO_2 in the latter compound is almost without influence on its spectrum. C. H. D.

Coloration of Mixtures of Anilines with Aromatic Nitro-compounds. E. von Biron and (Mlle.) O. M. Morguleva (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1598—1613).—The coloration produced on mixing aromatic amines with nitro-derivatives is regarded by Noelting and Sommerhoff (A., 1906, i, 157) and by Ostromisslenski (A., 1911, ii, 195, 476) as due to the formation of compounds between the components of the mixtures.

The authors have investigated spectrometrically and colorimetrically sixteen such mixtures, each containing one of seven different

aromatic amines, and either nitrobenzene or *o*- or *m*-nitrotoluene. On the assumption that the colour is due to the formation of a compound containing one molecule of each of the two constituents, the intensity of the colour should be proportional to the amount of the compound formed, and should follow the law $J=4x(1-x)$, where J is the ratio of the intensity of the colour to the maximum intensity. This law is obeyed accurately by mixtures of dimethylaniline and *m*-nitrotoluene, and approximately by dimethylaniline-*o*-nitrotoluene and ethylaniline-nitrobenzene. With the remaining mixtures, the curves are displaced to the right or left, so that the maximum coloration corresponds with more or less than 50 mol. % of the amine. Ostromisslenski's spectrophotometric measurements of mixtures of aniline and nitrobenzene showed that the maximum absorption corresponds with $x=0{\cdot}5$, but the cooling curve of the system does not indicate the formation of a compound, and the authors regard the existence of the compound, $Ph{\cdot}NO_2,NH_2Ph$, as not proved.

The coloration-composition curves show that, with different mixtures, the maximum coloration corresponds with concentrations of the amine varying from about $x=0{\cdot}3$ to $x=0{\cdot}65$, and that the position of the maximum is influenced more by the composition and structure of the amine than by those of the nitro-compound. Consequently, it would be necessary, supposing the coloration to depend on the formation of a compound, to make the improbable assumption that the compositions of such compounds vary in almost every case; further, in many cases the compositions would scarcely correspond with stoicheiometrical proportions.

A connexion appears to exist between the displacement of the coloration-composition curve and the relative volumes of the components of the mixture. When the molecular volume of the nitro-compound is greater than that of the amine, the maximum usually, but not invariably, corresponds with a solution containing more than 1 mol. of the amine per mol. of the nitro-compound, and inversely.

All the mixtures containing nitrobenzene are more highly coloured than those containing *m*-nitrotoluene, and these more highly than mixtures in which *o*-nitrotoluene occurs. The proximity of the methyl- and nitro-groups in the ortho-position apparently weakens the influence of the nitro-compound on the amine.

T. H. P.

The Absorption Spectra of the Vapours and Solutions of Anisole, Phenetole and Various Derivatives. JOHN EDWARD PURVIS (T., 1915, **107**, 660—667).—The influence of substitution in the benzene nucleus on the nature of the light absorption has been further examined by comparative observations on the absorption of anisole, *p*-bromoanisole, phenetole, *p*-fluorophenetole, *p*-bromophenetole, *o*- and *p*-anisidines, *o*- and *p*-phenetidines, *p*-azoxyanisole and *p*-azoxyphenetole.

The results obtained with anisole and phenetole show that the introduction of an aliphatic group does not alter the character of

the absorption, although the bands are not so sharp as those of phenol. When fluorine or bromine is introduced in the nucleus, there is a diminution in the number of the finer bands. The bands observed are much wider and more diffuse, especially in the bromine derivatives. This is supposed to be due to the damping and neutralisation of the fundamental oscillations of the nucleus. When the amino-group is introduced, the complex oscillations are completely neutralised, and a single large absorption band takes the place of the numerous bands exhibited by aniline and phenol.

The absence of the vapour bands from the solution spectra, and the greater width and diffuseness of the solution bands, are supposed to be the result of an association of the molecules brought about by the solvent. The effect of this is more obvious when two benzene groups are present in the molecule, as in the azoxy-compounds. These have a simpler absorption spectrum than that shown by anisole or benzene. H. M. D.

The Absorption Spectra of the Isomerides of Ammonium *d*-α-Bromocamphor-β-sulphonate. JOHN EDWARD PURVIS (T., 1915, **107**, 643—644).—The two isomerides of ammonium *d*-α-bromocamphor-β-sulphonate described by Pope and Read (T., 1914, **105**, 800), for which $[M]_{n_g\ 5461}=371°$ and 176° respectively, show no difference either in their general or specific absorptions. It is suggested that the rotation has its origin in the spaces and stresses between the asymmetric carbon atom and the groups of atoms with which it is in combination, whereas specific and general absorption are produced by electronic vibrations set up by the radiant energy from the source of light. The supposition that the CO-group is the primary centre of oscillation is supported by the fact that camphoroxime has no specific absorption band in the ultra-violet region. H. M. D.

Absorption Spectra and Constitution of Benzene Derivatives. V. Dialdehydo-, Dinitro-, and Aldehydonitrobenzenes. N. A. WALIASCHKO and (Mlle.) M. V. BOLTINA (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1741—1780).—It has been shown (A., 1910, ii, 1015; 1911, ii, 2) that, in many of its derivatives, the benzene nucleus exists in the isomeric α- and φ-conditions. The phenolic φ-structure occurs, preferably, in compounds containing the auxochrome groups, Me, OH, OMe, and NH_2, in immediate union with the carbon atoms of the benzene ring (A., 1914, ii, 231). This condition of the benzene nucleus is characterised by a spectrum with a single, more or less wide and deep, band, with the maximum absorption between $1/\lambda=3200$ and 3800. In cases where an unsaturated atom or atomic grouping is connected with the benzene nucleus by way of some other atom, as in the chromophoric groups, CHO, NO_2, etc., the α-form of the benzene ring predominates, the spectrum in this instance being characterised by two absorption bands, α_1 and α_2, with maxima at 3700—4000 and 2950—3200 respectively.

Investigation of the absorption spectra of *o*-, *m*-, and

p-dialdehydo-, dinitro-, and aldehydonitro-benzenes shows that these contain three bands, and that in all cases the character of the absorption of the mono-substituted derivative, benzaldehyde in the first instance and nitrobenzene in the last two, is maintained. Since the molecules of these mono-substituted compounds oscillate between the α- and ϕ-forms, the same should be the case with the disubstituted derivatives. The influence of the introduction of the second aldehydic or nitro-group is exerted principally in changing the intensity of the absorption, and only comparatively slightly in displacing the bands towards one or the other end of the spectrum; their effect is consequently similar to that of a methyl or acetyloxy-group (A., 1911, ii, 2). The second aldehydic or nitro-group, however, influences greatly the intensity of the α_2-band in all three isomerides, and that of the α_1-band in meta-derivatives, whilst the methyl and acetyloxy-groups, owing to their auxochromic character, assist more especially the development of the phenolic band with the meta- and para-isomerides.

In the dihydric phenols and the phenylenediamines, the similar auxochrome groups give absorption spectra of the phenolic type, and consequently resembling those of the corresponding mono-substituted derivatives, phenol and aniline, the influence of the second group being shown only in the changed intensity and displacement towards the red end of the spectrum of the ϕ-band. When different auxochromes are present, as in the *o*- and *p*-anisidines and in *p*-aminophenol, the spectra retain the phenolic type of absorption (compare Baly and Ewbank, T., 1905, **87**, 1353). These relations are similar to those now found for similar or different anti-auxochromic or chromophoric groups, CHO and NO_2. Thus, a second chromophoric, or even a strong auxochromic, group exerts only a feeble auxochromic influence on the benzene ring, the general character of the absorption being essentially that of the monosubstituted derivative. Only by a combination in the benzene ring of the chromophoric groups, CHO and NO_2, with the strong auxochromic groups, OMe, OH, ONa, or NH_2, is a change wrought in the type of the absorption, in consequence of particularly marked one-sided development of the α_2-band with ortho-isomerides, or of the phenolic band with para-isomerides, and of a more or less considerable displacement of the absorption towards the red end of the spectrum; the meta-isomerides occupy an intermediate position, but are the nearer in their spectra to the ortho-compounds.

It has been pointed out previously that these changes are not conditioned by quinonoid rearrangement, and this view is now confirmed by examination of the absorption spectra of the salts of the *aci*-nitro-compounds. The formation of the sodium salt with one nitro-group of *m*-dinitrobenzene and with the two nitro-groups of *o*-dinitrobenzene, is accompanied by displacement of the α_2-absorption band towards the red by $1/\lambda$ 1200—1400; when the salts of *m*- and *o*-nitrophenols are formed, the change amounts to $1/\lambda$ 500—650 in the same direction.

According to their relative positions, the aldehydo- and nitro-

groups exhibit varying reactivities. The most nearly equilibrated systems with the least reactive groups are *m*-dialdehydo- and *m*-dinitro-benzenes. The ortho- and para-isomerides, on the other hand, show a certain tension in their molecules and increased reactivity of their substituent groups, the second group, under the influence of an alkyloxide, striving to approach the auxochromic group, as in terephthalaldehyde, or even replacing the auxochromes by alkyloxy-groups, as with the dinitrobenzenes; these molecules thus tend to form more stable ring systems with chromophoric and auxochromic groups. T. H. P.

Absorption Spectra and Constitution of Benzene Derivatives. VI. Tautomerism of Acetanilide. N. A. WALIASCHKO and (Mlle.) M. V. BOLTINA (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1780—1787. Compare preceding abstract).—The authors have compared the absorption spectra of acetanilide, methylacetanilide, which is known to possess the normal structure, acetanilide methyl ether and ethenyl-*o*-phenylenediamine. The spectral curve of acetanilide resembles that of methylacetanilide far more closely than it does that of acetanilide methyl ether, the amidic structure of free acetanilide being thus confirmed.

The upper part of the curve for acetanilide in alkaline solution occupies a position intermediate to those of the curves for acetanilide in neutral alcohol and for acetanilide methyl ether, being nearer to the curve for the latter. According to Hantzsch (A., 1897, i, 399), in the formation of salts of acid amides, the sodium hydroxide or ethoxide first combines, with formation of an unstable product, $NH_2 \cdot CR(OEt) \cdot ONa$, this then losing water or alcohol and giving $NH{:}CR \cdot ONa$, in which the metal is united to oxygen. That this is the case, excepting in a few instances, is shown also by Wheeler's results (A., 1900, i, 492). The conclusion is therefore drawn that, in a 2*N*-solution of acetanilide in *N*-sodium ethoxide solution, the acetanilide is partly converted into the salt, with formation of the imidic modification, whilst 0·002—0·0002*N*-solutions of acetanilide in sodium ethoxide solution of normal concentration may contain only the initial product of combination with the alkyloxide.

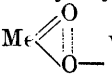
Thus, in neutral alcoholic solution, acetanilide possesses only the amidic structure, whereas in alkaline solution in presence of excess of alkyloxide it may undergo partial conversion into the imidic type, with formation of the salt.

The ordinary amidic formula for acetanilide, NHPhAc, does not, however, explain the anti-auxochromic action of the acetyl group, since, according to this formula, the carbon atom of the carbonyl group is strongly saturated by the oxygen atom, and cannot acquire any marked affinity from the nitrogen. The spectroscopic data are in best accord with the formula,

$$CMe\lessdot{\overset{O}{\underset{NHPh}{\|}}},$$

proposed by Smedley (T., 1909, **95**, 233) to explain the low refractometric constant of nitrogen in acid amides. T. H. P.

Absorption Spectra and Constitution of Benzene Derivatives. VII. Mono- and Di-acetoxybenzenes, Phenylenediamines and their Diacetyl Derivatives, and Certain ω-Derivatives of Toluene. N. A. WALIASCHKO and (Mlle.) M. V. BOLTINA (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1788—1822. Compare preceding abstracts).—The results obtained previously lead the authors to suppose that atoms or groups requiring from the carbon atoms of the benzene nucleus more affinity than a hydrogen atom lead to a phenolic structure of the molecule, characterised by a more or less highly developed absorption band. It is assumed, further, that each atom possesses a definite amount of affinity, distributed between its linkings with other atoms. If one of the latter requires a large quantity of affinity, less will naturally remain for the others. Consequently, any change in the degree of saturation of a group will be felt in its influence on the benzene ring and on the absorption spectrum, and it may be expected that a sufficiently strong mutual action between the substituent groups will result in the conversion of an absorption spectrum into one of another type. These considerations have been applied to the study of the more or less highly saturated character of the meta-orientated or chromophoric groups. Two cases are examined: (1) the depression of the influence of strongly auxochromic groups by saturation of their atoms by acetyl groups, as shown in the absorption spectra of the acetyl derivatives of mono- and di-hydric phenols and mono- and di-aminobenzenes; (2) the absorption spectra of certain toluene derivatives obtained by replacing the hydrogens of the methyl group by more or less marked auxochromes, as, for instance, in the conversion of the feeble auxochromic methyl group into the chromophoric aldehydic group.

In the case of acetoxybenzene, the influence of the acetoxy-group results in the appearance of the α_2-band, the absorption spectrum approximating to the benzaldehyde type. Introduction of a second acetoxy-group in the meta-position causes marked intensification of the α_2-band, just as in the conversion of benzaldehyde into *m*-dialdehydobenzene. From the results obtained with dialdehydo- and dinitro-benzenes, it would be expected that the ortho- and para-isomerides would exhibit still greater development of the α_2-band, the type of the absorption being that of the monosubstituted compound. This is, however, not the case, since the α_2-band is not intensified in the ortho- and para-compounds, but with *o*-diacetoxybenzene is only one-third as strong as in acetoxybenzene. The conclusion is drawn that the acetoxy-groups must differ in some way, and it is supposed that these groups have a structure similar to that suggested for the carboxyl group by Smedley (T., 1909, **95**, 231; compare Brühl, T., 1907, **91**, 115), and assumed also by Lowry and Southgate (T., 1910, **97**, 912) and by Bielecki and Henri (A., 1914, ii, 7) for the carbonyl group of ketones. Only by assuming the acetoxy-group to have the structure  with neutralised residual valencies is it

possible to explain the known anti-auxochromic influence of acetylation, since, according to the ordinary configuration, the hydroxylic oxygen is combined with an already saturated carbon atom, and should, therefore, possess a large store of residual affinity. According to the formula $C_nH_{2n+1}\cdot C\langle{}^{O\cdots}_{O}\rangle K$, assigned by Hantzsch and Scharf (A., 1914, ii, 5) for salts of acids, the residual affinity of the carbonylic oxygen is satisfied by the group combined with the carboxyl. In the cases here considered, this formula is quite inapplicable, as such a carboxyl group should take from the carbon atom of the ring more affinity than a hydrogen atom, and should therefore have a stronger auxochromic effect. It is supposed, then, that acetoxybenzene has the structure

$$CH_3\cdot C\langle{}^{O}_{O\cdot Ph}\rangle,$$

and the occurrence of such groupings in the meta-position would favour the anti-auxochromic action. With the ortho- and para-isomerides, the positions are less favourable, the carbon atoms of the ring requiring more affinity from the hydroxylic oxygen, so that more or less neutralisation of the residual affinities by the carbonylic oxygen would prevail; these groups would then approximate to the ordinary formula, and the phenolic condition would predominate in the molecule.

The conversion of aniline into acetanilide is accompanied by a change in the absorption spectrum similar to that observed when phenol undergoes an analogous transformation, except that the α_2-band is less sharply marked, the ϕ-band is diminished fourfold in comparison with phenol, and the α_1-band, already present with aniline, shows increased development, and is imposed on the phenolic band.

Considerations similar to those given above for the acetoxybenzenes are valid also with the diacetyl derivatives of the phenylenediamines. The groups $CH_3\cdot C\langle{}^{O}_{O\cdot}\rangle$ and $CH_3\cdot C\langle{}^{O}_{NH\cdot}\rangle$ exert similar effects on the benzene ring, these effects being greater in the meta-disubstituted derivatives than in the monosubstituted compound, and greater still in the ortho- and para-isomerides, with which the phenolic constitution predominates.

The absorption spectra of toluene, benzyl chloride, benzylidene chloride, benzotrichloride, benzylamine, and benz*anti*aldoxime have also been investigated. The results show that replacement of the hydrogen atoms of the methyl group in toluene by groups of unsaturated atoms, or groups taking from the methane carbon atom more affinity than hydrogen does, is accompanied by change of the absorption spectrum of the toluene in the direction of the benzaldehyde type. This effect is weak in the case of chlorine, of which, at least, two atoms are required, whilst a single hydroxyl or amino-group is sufficient to cause the change. Introduction of a second hydroxyl group, or replacement of two hydrogen atoms

of the methyl by an oxygen atom or a hydroxyimino-group, merely causes considerable intensification of the absorption without altering its type. By replacement of the oxygen atom of benzaldehyde by two acetoxy-groups, part of the affinity of the oxygen is removed, and the absorption exhibits diminished intensity, but is unaltered in type. If, as occurs when benzylamine and benzaldoxime form salts, the saturation of the substituent groups goes so far that the groups require less affinity than hydrogen does from the methyl carbon atom, and so render this more unsaturated than in toluene, the type of the absorption undergoes change, with formation of the phenolic band (compare "inversion of auxochromes," Kaufmann, "Die Valenzlehre," Stuttgart, 1911, 522).

The results described in earlier papers show that the series of changes represented by the scheme

$C_6H_6 \longrightarrow C_6H_5Me \longrightarrow Me{\cdot}C_6H_4Me \longrightarrow Ph{\cdot}OMe \longrightarrow Ph{\cdot}OH$

corresponds with a gradual change in the character of the absorption spectrum. It is now evident that similar relations hold for the series $C_6H_6 \longrightarrow Ph{\cdot}CH_2{\cdot}OH \longrightarrow Ph{\cdot}CH(OEt)_2 \longrightarrow Ph{\cdot}CHO$ and $C_6H_6 \longrightarrow Ph{\cdot}CH{\cdot}NH_2 \longrightarrow Ph{\cdot}CH{:}N{\cdot}OH$. It may be supposed that the two established types of absorption spectrum enter, in a very feeble form, into the composition of the benzene spectrum, and that, in addition to vibrations constituting the unbroken ring of the benzene molecule, the latter exhibits other vibrations which are developed in three groups, corresponding with the α_2-, ϕ-, and α_1-bands. Introduction of substituents into the nucleus produces more or less marked intensification and retardation of the vibrations. Groups requiring more affinity than hydrogen are characterised by vibrations giving the phenolic absorption band, the other vibrations being changed in one or the other direction in so far as they are connected with the first; the spectra obtained are of the phenolic type, sometimes with the α_1-band. If the substituent groups require less affinity than hydrogen, intensification and retardation of all three groups of vibrations occur, with formation of absorption spectra containing three bands. T. H. P.

Absorption Spectra and Constitution of Benzene Derivatives. VIII. Benz*anti*aldoxime and Benz*syn*aldoxime. N. A. Waliaschko (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1822—1830. Compare preceding abstracts).—The spectra of the two isomeric benzaldoximes do not give identical curves, and the results of Stewart's investigations with mesaconic and citraconic acids, according to which the more symmetrical molecule shows the greater absorptive power (T., 1907, **91**, 208; compare also Magini, A., 1904, ii, 107), are confirmed only as regards part of the curves. As far as nearly $1/\lambda\,100$, the *syn*-oxime exhibits the greater absorption, but with a thickness of about 10,000 mm. the curves intersect, the *anti*-oxime showing the greater absorption in the region of the ϕ-band, and displacement of the α_1-band towards the red end of the spectrum. The greater absorption of the *syn*-oxime in the upper part of the curve probably corresponds with the lack in the spectra of the oximes of the α_2-band of benzaldehyde.

These differences in intensity and position of the bands are increased under the influence of varying proportions of sodium ethoxide. This observation is in agreement with Hantzsch and Hartung's investigations on the isomeric benzilmonoximes and *p*-nitrobenzaldoximes (A., 1910, i, 474), but the explanation advanced by these authors is inapplicable in the present case, since the isomeric benzaldoximes contain no negative groups. The most probable explanation is furnished by Beck and Hase's view (A., 1907, i, 825), according to which *syn*-aldoximes are capable of existing in two tautomeric forms, $\begin{matrix}R\cdot C\cdot H\\ \|\\ N\cdot OH\end{matrix}$ and $\begin{matrix}R\cdot C\cdot H\\ |\\ NH-\end{matrix}\!\!>O$, the latter being preferred (compare Forster and Dunn, T., 1909, **95**, 425; Nelson and Falk, A., 1909, i, 349). T. H. P.

The Fluorescence and Resonance Radiation of Sodium Vapour. I. Hon. R. J. Strutt (*Proc. Roy. Soc.*, 1915, [*A*], **91**, 388—395).—It has been shown previously (compare A., 1914, ii, 599) that sodium vapour, which has been stimulated to emit the line spectrum by electric discharge, carries its luminosity over a distance of several centimetres when the vapour is distilled away from the region of discharge. The resonance radiation excited by the light emitted from a sodium flame is not sufficiently persistent, however, to be carried along when the vapour is distilled away from the region of excitation. This difference in the behaviour of the emission centres emphasises the distinction between electrical and fluorescent excitation. The behaviour of sodium vapour is in striking contrast with that of mercury vapour, for it has been found that the line λ 2536 of mercury persists for some time, whether it is excited optically or electrically.

The resonance radiation of sodium vapour is absorbed completely by a layer of sodium vapour which is quite transparent to white light.

If the excited vapour is placed in a magnetic field, the resonance radiation changes in intensity. With an exciting flame of low intensity, the radiation diminishes with increasing strength of the field, but if the exciting flame is of high intensity, the radiation increases to a maximum, and then diminishes.

Changes in the intensity of the resonance radiation are also observed if the exciting flame is acted on by a magnetic field. The magnetic field reduces the radiation if the exciting source is weak, and increases the radiation if the sodium flame is of high intensity.

The magnetic effects can be explained in terms of the Zeeman resolution of the *D*-lines, and the width and structure of these lines as emitted by the flames used in the experiments. H. M. D.

Pasteur's Principle of the Connexion Between Molecular and Physical Asymmetry. I. F. M. Jaeger (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1217—1236).—The author discusses the significance which must be attached to the term molecular asymmetry and the conditions which determine the occurrence of

mirror-image isomerides and the formation of enantiomorphic crystals. According to Werner (compare A., 1912, i, 166), molecular asymmetry is not primarily determined by the inequality of the substituents, but by the spacial arrangement. With this idea in view, the author has investigated the optical activity of the luteo-triethylenediaminecobaltic salts of the type $[Co\ en_3]X_3$, where en represents $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, including the *d*- and *l*-bromides, iodides, nitrates, perchlorates, and thiocyanates. The salts are characterised by very high rotation dispersion, but change of temperature has little influence on the rotating power. The rotation of the bromides, iodides, and perchlorates is greater than that of the nitrates and thiocyanates.

Crystallisation experiments have shown that the *d*- and *l*-salts yield hemihedric crystals in the case of the nitrate and perchlorate, but no evidence of hemihedry was obtained with the other salts examined. On the contrary, the crystallographic evidence afforded by the iodides and thiocyanates favours the view that the two antipodes are holohedral.

The observations indicate that the asymmetric spacial configuration, although always associated with optical activity, is not of necessity accompanied by enantiomorphism of the crystalline forms. It is supposed that the optical activity is mainly determined by the spacial configuration, whilst the enantiomorphism is dependent on chemical differences in the substituents. The case of a compound containing an asymmetric atom is particularly favourable to the appearance of both properties. H. M. D.

The Distribution of Energy in the Radiation from the Uviol-glass Lamp. ARTHUR JOHN ALLMAND (T., 1915, **107**, 682—688).—The distribution of energy in the radiation emitted by a Schott mercury Uviol-glass lamp has been determined by direct measurement of the intensity of the different bands by means of a thermopile. The light was resolved by means of a Hilger monochromatic illuminator, and the thermopile current measured with the aid of a Paschen galvanometer.

The intensities of the bands, referred to the blue band = 1, are compared with the corresponding values (in brackets) obtained by Winther, who used a fluorometer for the energy measurements (A., 1913, ii, 458). The numbers obtained are: λ 571 μμ, 0·27, (—); λ 541, 0·73, (—); λ 436, 1·00, (1·00); λ 405, 0·56, (0·29); λ 362, 0·42, (0·25); λ 313, 0·17, (0·045). On comparison of the results with those obtained for the quartz lamp by Ladenburg (*Physikal. Zeitsch.*, 1904, **5**, 525), it is found that the relative intensities of the blue (λ 436) and violet (λ 405) bands are approximately the same for the two lamps, but that the intensities of the ultra-violet and of the green and yellow bands relative to the blue are much smaller for the Uviol than for the quartz lamp.

By applying the results to the data obtained by Luther and Forbes (A., 1909, ii, 632) in the investigation of the photochemical oxidation of quinine by chromic acid, it is found that the ratio of the intensities of the bands λ 406 and λ 362 is 1·00 : 0·75, which is

in good agreement with the corresponding ratio of the velocity-coefficients, 1·00 : 0·82. This would seem to show that the reaction velocity is proportional to the absorbed energy, and independent of the frequency of the light. H. M. D.

The Absorption of Homogeneous β-Rays. R. W. VARDER (*Phil. Mag.*, 1915, [vi], **29**, 725—733).—A powerful beam of approximately homogeneous β-rays of known velocity was obtained by arranging a tube of radium emanation and two slits on the circumference of a circle in a known uniform field. The absorption in aluminium of rays of various velocities was observed. An approximately linear relation was found to hold between the ionisation and the thickness of aluminium traversed, and the thickness of aluminium at which the radiation is completely absorbed may be considered the "range" of the β-rays. The range varies approximately linearly from about 0·01 cm. for rays for which $H\rho$ is 2000 to 1·4 cm. for rays for which $H\rho$ is 11,500. The linear character of the absorption curve in aluminium results from a chance balancing of the scattering of the β-particles and the diminution of their velocity. In the case of paper, where scattering is small, the absorption curve is concave; in the case of platinum and tin, where the scattering is large, the absorption curve is convex towards the origin. The results, as regards the range of the β-rays, are considered with reference to a mathematical theory worked out by Bohr. F. S.

Absorption in Lead of the γ-Rays Emitted by Radium-*B* and Radium-*C*. H. RICHARDSON (*Proc. Roy. Soc.*, 1915, [*A*], **91**, 396—404. Compare Rutherford and Richardson, A., 1913, ii, 461).—The curves representing the absorption of the γ-rays emitted by radium-*B* and -*C* have been determined. Analysis of the curves shows that the radiation from radium-*B* consists of three types, for which $\mu = 1·5$, 6·0, and 46 respectively. The percentage ionisation produced in methyl iodide vapour by these three groups of rays was found to be 12, 26, and 62 respectively. In the case of radium-*C*, it was found that about 85% of the ionisation was due to very penetrating rays, for which $\mu = 0·5$, the residual effect being due, apparently, to rays of the same character as those emitted by radium-*B*.

The investigation of the absorption of the rays in elements of high atomic weight has shown that the rays behave differently from the characteristic rays emitted by elements of low atomic weight. The absorption coefficient is not abnormally high when the atomic number of the absorber is slightly less than that of the element emitting the radiation. H. M. D.

The Corpuscular Radiation Liberated in Vapours by Homogeneous *X*-Radiation. H. MOORE (*Proc. Roy. Soc.*, 1915, [*A*], **91**, 337—345).—In a previous paper (A., 1914, ii, 88), it has been shown that the number of corpuscles given out by an atom

of carbon or oxygen under the influence of X-rays is the same, whether the atom is in combination or not. Further experiments have been made to ascertain whether this relation holds good for other elements.

The corpuscular radiation which is liberated per centimetre by a homogeneous (copper) X-ray beam of unit intensity has been determined by observations on nitrous oxide, carbon dioxide, ammonia, carbon disulphide, chloroform, hydrogen chloride, and carbon tetrachloride. The values, when reduced to a gas pressure of 76 cm., show the existence of additive relations in that the corpuscular radiation in a gas (air = 1) can be represented as the sum of the atomic corpuscular radiations of the constituent elements. The atomic constants (atomic corpuscular radiations) have the following values: carbon, 0·2; nitrogen, 0·34; oxygen, 0·62; sulphur, 10·9; chlorine, 14·7. These numbers are approximately proportional to the fourth power of the atomic weights.

Since recent observations have shown that the coefficient of absorption of a beam of X-rays in a gas is proportional to the quantity of corpuscular radiation emitted, it follows that the X-radiation absorbed by an atom will also be proportional to the fourth power of its weight. Since the above relation between the X-ray absorption and the emission of corpuscular radiation also holds for solid elements, it should be possible to calculate the absorption coefficient for any substance provided its homogeneous radiation is not excited. H. M. D.

The Effects of Different Gases on the Electron Emission from Glowing Solids. Frank Horton (*Proc. Roy. Soc.*, 1915, [*A*], **91**, 322—337. Compare A., 1914, ii, 794).—Further experiments have been made to test the theory that the emission of electrons from strongly heated substances is due to chemical action (compare Fredenhagen, A., 1913, ii, 903; Gehrts, *ibid.*, 1005). With this object in view, measurements have been made of the ionisation produced by Nernst filaments heated in air, oxygen, nitrogen, and hydrogen. The filaments were heated by means of an alternating current at 1525°, and the variation of the thermionic current with the pressure of the surrounding gas for a fixed difference of potential, and also the variation of the current with the potential difference at constant gas pressure, were observed.

At low pressures, the thermionic current from a given filament is practically independent of the surrounding gas. The fact that the electron emission has the same value in oxygen and in hydrogen is considered to prove that the phenomena cannot be attributed to chemical action between the heated cathode (the Nernst filament) and the gas surrounding it.

At higher temperatures, the thermionic currents vary considerably, but this is attributable to the production of ionisation by the collision of gas molecules.

In the case of a platinum cathode, hydrogen seems to exert a definite influence in that the electron emission is greatly increased

by this gas. This effect is probably connected with the fact that hydrogen is absorbed by the platinum. H. M. D.

An Investigation of the Photographic Effect of Recoil Atoms A. B. Wood and A. I. Steven (*Proc. Physical Soc., London*, 1915, **27**, 189—192).—Since the ionising, phosphorescent and photographic action of α-rays cease together, and are probably all due to the same cause, and since the recoil-atoms possess strong ionising power, the attempt was made to see if the latter would affect a photographic plate. Polonium was used, since its recoil-atom is inactive. Examination of the effects produced (1) by both α-particles and recoil-atoms in a vacuum, (2) by α-particles alone, the recoil-atoms being absorbed by gas in the apparatus, showed a slightly denser image in the former case, but the effect may be due to the scattering of the α-particles in the latter case. In a second method, both α-particles and recoil-atoms were magnetically deviated. It is known that the former are deviated to twice the extent of the latter. No effect of the recoil-atoms on the photographic plate could be detected. Schumann plates, consisting of a thin film of silver chloride on glass, as well as ordinary gelatin-coated plates, were tried. So experiments designed to detect a phosphorescence by the recoil particles on a zinc sulphide screen also gave inconclusive results. F. S.

Lead and the End Product of Thorium. II. Arthur Holmes and Robert W. Lawson (*Phil. Mag.*, 1915, [vi], **29**, 673—688. Compare this vol., ii, 5).—A careful selection of preceding analyses and a variety of assumptions lead to the conclusion that the half-period of thorium-*E*, the isotope of lead derived from thorium, is about a million years. The question whether bismuth is an end-product of the thorium series is discussed at length, as also are the atomic-weight determinations carried out on the lead from radioactive minerals, the nature of the possible end-product of the actinium series, and the problem of determining the geological age of minerals. F. S.

A New Type of Ion in the Air. J. A. Pollock (*Phil. Mag.*, 1915, [vi], **29**, 636—646).—The characteristics of an ion in the air, having a mobility intermediate between that of the small gas ion and the large Langevin ion, are discussed. Below a pressure of water vapour of 17 mm., both intermediate and large ions co-exist in air, but above 17 mm. only the large ion is found. The mobility of the new ion is a function of the water-vapour pressure rather than of the relative humidity, and decreases rapidly with increase of the vapour pressure. It is suggested that the intermediate ion consists of a rigid nucleus enveloped by a dense atmosphere of water vapour. At a certain critical pressure, the vapour adsorbed assumes the liquid state, rapid condensation ensues, and the large ion is produced. The intermediate ion is a striking illustration of the two modes of condensation of water vapour (Trouton, *Proc. Roy. Soc.*, 1907, **79**, 383), the latter condensing on solid surfaces first as an atmosphere of water molecules,

which, at a certain degree of humidity of the atmosphere, changes abruptly to the liquid condition. F. S.

Electromagnetic Inertia and Atomic Weight. J. W. NICHOLSON (*Proc. Physical Soc., London*, 1915, **27**, 217—229).—By mathematical reasoning, a formula is deduced for the combined mass of two electrical charges when in proximity to one another. If it be supposed that the mass is of electromagnetic origin, both for the positively as well as the negatively charged parts of the atom, the mass is not the sum of the masses of the individual charges when far apart. For two charges e_1, e_2, of radii a_1, a_2 at distance apart λ, the mass is given by $2/3c^2(e_1^2/a_1+e_2^2/a_2+3e_1e_2/\lambda)$ (that for a single charge being $2/3c^2(e^2/a)$), where c is the velocity of light. The mass increases when two charges of like sign are brought closer, but decreases if the signs of the charges are opposite. The above result can be extended to any number of charges. In the production of one isotope from another by the expulsion of one α- and two β-particles, the atom should suffer a loss in mass less than that of the helium atom expelled, but the difference is very small. When, in course of radioactive changes, the product occupies a place in the periodic table different from that occupied by the parent, the change of mass should be much greater. It is calculated that the atomic weight of lead derived from radium should be less than the calculated value, 205·98, by $1{\cdot}65\ a/\lambda$, where a is the radius of the electron and λ is the mean distance between the α-particles in the atom. In the case of lead from thorium, the difference should be $2{\cdot}40\ a/\lambda$. From a value given by Soddy (*Nature*, February 4th, 1915) for the atomic weight (? density) of lead from thorite, 207·64, it is calculated that λ/a in the thorium atom is approximately 3. Thus, the mean distance apart of the α-particles in a thorium atom appears to be comparable with the radius of the electron. On the supposition that all lead is derived from thorium and uranium, the atomic weight, 207·10, leads to the view that three-quarters is derived from thorium and one-fourth from uranium. Other deductions from the formula are considered. F. S.

The Decomposition of "Crude Sulphates" in the Preparation of Radium by Calcium Carbide and Mixtures of Calcium Carbide and Calcium Hydride. E. EBLER and W. BENDER (*Zeitsch. anorg. Chem.*, 1914, **88**, 255—264. Compare A., 1913, ii, 546, 904).—Reduction of the sulphates with carbon is only complete when the mixture consists of nearly pure barium and radium sulphates. Crude products containing much silica are very imperfectly reduced. The powdered material is heated with powdered carbon, and rapidly added to hot dilute hydrochloric acid, hydrogen sulphide being expelled as rapidly as possible by boiling.

Calcium carbide readily reduces the sulphates, approximately according to the equation $MSO_4+4CaC_2=4CaO+MS+8C$, much carbon being set free. The product is a pulverulent mass. Even the crude material containing much silica is well reduced.

The violence of the reaction with calcium hydride may be modified by using a mixture with calcium carbide, the quantity of the latter depending on the quantity of impurities in the sulphates. With barium and radium sulphates, only 75% of the hydride may be replaced by carbide. The yield is increased by reducing larger charges, up to 50 kilos., in one operation. C. H. D.

Behaviour of Radio-Elements in Precipitation Reactions. II. K. FAJANS and F. RICHTER (*Ber.*, 1915, **48**, 700—716. Compare A., 1913, ii, 1010).—In the earlier paper, the general rule was established that a radio-element is carried down from an extremely dilute solution with a precipitate of an ordinary element if, under the conditions, the radio-element itself would be precipitated if it were present in sufficient concentration. The subject has now been investigated more thoroughly in the case of thorium-*B*.

It is again shown that there is a close connexion between the completeness of the removal of the active element and the solubility of its salt. Thorium-*B* is almost completely carried down with bismuth sulphide, manganese carbonate or barium sulphate, to the extent of 30—40% with silver haloids, and scarcely at all with nitron nitrate, which agrees, in the above sense, with the solubilities of the sulphide, carbonate and sulphate, haloids and nitrate of the congener, lead. If the ordinary metal is incompletely precipitated, the active element is only partly carried down. The degree of the precipitation also depends on the solubility of the precipitate of the ordinary element. Whereas thorium-*B* is almost completely carried down with manganese or barium carbonate, only a small amount is removed when ammonium carbonate is precipitated by ammonia or crystallised from a saturated solution.

An important fact is established, that the precipitation of the radio-element is not so much governed by the nature of the ions in solution as by the negative part of the precipitate. Thus, even in a solution containing ammonium sulphate, nitron nitrate does not carry down any appreciable quantity of thorium-*B*, whilst the precipitate of basic ferric acetate, made by adding ferric nitrate, and then ammonium acetate, to the active solution, removes the whole of the radio-element.

When the precipitate is the insoluble salt of an isotope, the removal of the radio-element is due to solid solution (compare this vol., ii, 207), whereas the removal by precipitates of non-analogous elements is due to adsorption. Thus, scarcely any thorium-*B* can be washed out of a precipitate with lead chloride by a solution of lead chloride, whereas freshly precipitated silver chloride, when added to an active solution, carries down scarcely any of the active element, and the activity of a silver chloride precipitate, when produced in thorium-*B* solution, can be diminished by more than 90% by one washing with dilute hydrochloric acid.

The precipitation and adsorption of radio-elements, the formation of solid solutions, and the growth of crystals are discussed in

the light of modern theories (compare W. H. and W. L. Bragg, Haber and Paneth). J. C. W.

Radium Content of Water from the Gulf of Mexico. Stewart J. Lloyd (*Amer. J. Sci.*, 1915, [iv], **39**, 580—582).—A sample of sea-water taken in the Gulf of Mexico about 200 miles south of Mobile, Ala., contained $1{\cdot}7 \times 10^{-12}$ gram of radium per litre. This figure is in comparative agreement with those recorded by Eve and by Satterly (A., 1909, ii, 633; 1912, ii, 118), but differs from the results given by Joly (A., 1909, ii, 780). W. P. S.

Electrical Conductivity of Mixtures of Fused Salts. C. Sandonnini (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 616—621).—The conductivities at 500°, expressed in reciprocal ohms, and the melting points of the separate salts used in these experiments, are found to be as follows: lead chloride, 1·472, 495°; lead bromide, 1·030, 368°; silver chloride, 3·654, 455°; silver bromide, 2·920, 422°; thallous chloride, 1·224, 429°.

With the system $PbCl_2$–$PbBr_2$, the solidification diagram indicates the formation of mixed crystals of Roozeboom's first type (compare Mönkemeyer, A., 1906, ii, 604).—For all the mixtures, the conductivities at 500° are slightly lower than those calculated according to the law of mixtures, the difference reaching the maximum value, 4%, for the equimolecular mixture.

With AgCl–AgBr, which forms homogeneous mixed crystals of Roozeboom's second type (Mönkemeyer, *loc. cit.*), the conductivities are also lower than the calculated values, the maximum divergence being 1·27% for the equimolecular mixture.

The system TlCl–AgCl forms a compound decomposing on fusion (compare Sandonnini and Aureggi, A., 1912, ii, 162), and the maximum excess of the calculated over the observed conductivity is about 27%. In the preceding systems, these differences are to be attributed mainly to retrocession of the degree of dissociation owing to the presence of an ion common to the two salts, but in this case they are due principally to the existence of complex molecules in the fused mixtures.

Definite deductions cannot be drawn from the values of the specific conductivity, owing to possible variations in density of the two salts on mixing. From the measurements already made of the densities of the mixtures, it would appear that such variations are small, and incapable of altering the general course of the specific conductivity. T. H. P.

Reactions of Both the Ions and the Molecules of Acids, Bases and Salts. XIX. Conductivity and Ionisation of Sodium Ethoxide, Potassium Ethoxide, Lithium Ethoxide, Sodium Phenoxide, Lithium Phenoxide, Sodium Phenylthiourazole, Sodium Iodide, Sodium Bromide and Mixtures of these Electrolytes in Absolute Ethyl Alcohol at 0°, 25° and 35°. H. C. Robertson, Jun., and S. F. Acree (*J. Physical Chem.*, 1915, **19**, 381—432. Compare A., 1913, ii, 576, 577, 688, 748).—In their work on catalysis, the authors have had need of the

degree of ionisation of the substances mentioned above. They have therefore carried out a series of electro-conductivity measurements of these substances at 0°, 25°, and 35°. The ethyl alcohol used as solvent in these measurements was purified by boiling for some time with silver nitrate, and then distilling into quicklime, by which it was dehydrated in the usual manner. In this way, alcohol was obtained which contained amounts of water up to 0·04%. The best alcohol obtained in this way had a density D_4^{25} 0·785065, and various samples had specific conductivities between $0·07 \times 10^{-6}$ and $0·28 \times 10^{-6}$. The alcohol was preserved in large flasks, protected from the air by tubes containing phosphoric oxide and soda-lime. The measurements were effected in conductivity vessels specially designed, so that the chance of a change in the specific resistance capacity is reduced to a minimum. Twelve such cells of different construction are described in the paper, and drawings of these are given, together with experimental results demonstrating the absence of change in the specific resistance capacity. The electrodes were throughout the work of bright platinum, since it is shown that platinised electrodes effected changes in the solutions. The equivalent conductivity of the substances mentioned in the title have been determined at dilutions down to $1/131072N$, or to such dilution that the infinity value is obtained. The degree of ionisation is calculated in every case for all the dilutions measured, and the Ostwald constant deduced. The conductivity of the following mixtures has also been determined: sodium iodide and sodium ethoxide, sodium bromide and sodium ethoxide, sodium iodide and sodium ethoxide, sodium phenoxide and phenol, potassium phenoxide and phenol, lithium phenoxide and phenol, and sodium ethoxide and sodium phenoxide. A series of viscosity measurements of several of the substances mentioned in the title has been made at 25° and 35°, and at several concentrations. The temperature-coefficients of the equivalent conductivities of the very dilute solutions are practically the same for all the salts, and average 2·65% per degree between 0° and 25°, and 2·8% per degree between 0° and 35°. The temperature-coefficients of the concentrated solutions are somewhat larger, and vary considerably, with the different salts. Lithium ethoxide and lithium phenoxide in solutions more dilute than $N/2$ give a constant when the proper data are inserted in the Ostwald dilution formula. All the other electrolytes give values which gradually decrease as the concentrations decrease. The conductivities of mixtures of the electrolytes can be calculated by Barmwater's method (A., 1899, ii, 396) from the conductivities of the individual electrolytes, provided that the total concentration of the electrolytes is not more than $N/2$. The conductivities and the viscosities of the mixtures of N-solutions are less than those calculated by the same method. Electrolytes in ethyl alcohol solution cause a very much larger percentage increase in viscosity than the corresponding electrolytes in water. The viscosities of the mixtures examined are additive, provided that the total concentration is not more than $N/2$. Mixtures of N-solutions have viscosities smaller than those calculated in this

way. The conductivity and the viscosity data show that in alcoholic solutions which have concentrations less than $N/4$, the ratio μ_v/μ_∞ gives a closer approximation to the value of α than does the formula $\mu_v\eta_v/\mu_\infty\eta_\infty$ used by Noyes, Washburn, and others, although neither formula is correct for N- and $N/2$-solutions.

J. F. S.

Peculiarities of Electrical Conductivity in Mixed Solvents. A. G. Doroschevski and S. V. Dvorshantschik (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1676—1699. Compare A., 1913, ii, 1014; 1914, ii, 419, 610).—To solutions of strong electrolytes in mixtures of water and alcohol the same conductivity dilution formula is applicable as to solutions in water alone. Within narrow limits of dilution, use may be made of a linear formula of the type $\lambda = A - a/\sqrt[n]{v}$, where the value of n depends on the nature of the salt, and is 3 for potassium and sodium chlorides, 4 for barium chloride and nitrate, etc. From this dilution formula, it follows that λ/λ_1, expressing the ratio between the conductivities in water and in the mixed solvent, should depend on the concentration of the salt, so that the law of Lenz (*Mem. Acad. St. Petersburg*, 1882, **30**, and *Ann. Phys.*, *Beibl.*, 1887, **7**, 399) and Cohen (A., 1898, ii, 154) is inaccurate. The formula given by Arrhenius (A., 1892, 1038), $l = l_0(1 - ax/2)^2$, is also found to be invalid. Wakeman's formula, $\Delta/p(100-p) = k$ (A., 1893, ii, 257), is confirmed for various uniequivalent salts in mixtures of water and alcohol, and may be utilised in practice. Modification of Wakeman's formula to the form $\Delta^x/p(100-p) = k$, where x is a magnitude dependent on the nature of the salt, renders it applicable to solutions of barium chloride and nitrate in mixtures of water and alcohol.

T. H. P.

Electrical Conductivity and Diagram of State of the System Formed by Benzoic Acid with Pyridine. A. Baskov (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1699—1716).—The results obtained previously with the systems formed by aniline and *o*- and *p*-toluidines with benzoic acid (A., 1913, ii, 1016) rendered it of interest to investigate the electrical conductivities of systems exhibiting chemical compounds which correspond with distinct maxima of the melting point, and may be supposed to be so stable that they are not appreciably dissociated into their components, even at temperatures far beyond the melting points.

Such a system is pyridine–benzoic acid, which forms a definite compound composed of 1 mol. of each constituent, and corresponding with the maximum melting point, 43·7°. The system shows also two eutectics, one corresponding with 55 mol. % of benzoic acid and 42·8°, and the other with about 5 mol. % of the acid and a temperature of about −41°. In accord with the more markedly basic properties of pyridine, the compound formed is more stable than those given by benzoic acid with aniline and *o*- and *p*-toluidines.

The electrical conductivity of the system was investigated at

eleven different temperatures, ranging from 0° to 250°, the temperature-coefficient of conductivity being positive. The maximum of conductivity corresponds with about 66 mol. % of benzoic acid, and, on raising the temperature, is displaced towards the 50 mol. % point. The pyridine–benzoic acid complex which shows such high conductivity begins to dissociate at 125°, so that in the region of the greatest conductivity, where the concentrations are most suitable for the formation of the complex, the conductivity temperature-coefficient becomes negative above 125°; this negative coefficient attains its maximal value at about 66 mol. % of the acid. T. H. P.

The Behaviour of Sucrose in the Silent Discharge. WALTHER LÖB (*Biochem. Zeitsch.*, 1915, **69**, 36–38).—Sucrose undergoes hydrolysis under the influence of the silent discharge. S. B. S.

Electro-culture. I. The Influence of the Silent Discharge on Enzyme Actions. WALTHER LÖB and A. SATO (*Biochem. Zeitsch.*, 1915, **69**, 1—35).—Aqueous solutions of starch are hydrolysed under the influence of the silent and spark discharge in the absence of oxygen. A part, however, escapes hydrolysis, and is apparently polymerised, and this product is more resistant to the action of diastase than untreated starch. After electrical treatment, the diastatic properties of pancreatin are inhibited, as is also the action between diastase and starch. Silk peptone is only hydrolysed to a very small extent by the electrical discharge, and ammonia is a product of the action. Caseinogen and fibrin are also resistant to the action of the discharge. The tryptic reaction by pancreatin, and the reactions between the enzyme and caseinogen and fibrin, are inhibited by the discharge. The silent discharge causes hydrolysis of tributyrin, but weakens the action of pancreatic lipase. S. B. S.

Reproducibility of the Cadmium Electrode. FREDERICK H. GETMAN and VERNETTE L. GIBBONS (*J. Amer. Chem. Soc.*, 1915, **37**, 953—970).—This work was undertaken with the object of finding an explanation of the abnormalities observed by Getman (A., 1911, ii, 888) in determinations of the potential of cadmium rods in alcoholic solutions of cadmium iodide.

Measurements of the *E.M.F.* of concentration cells of solutions of cadmium iodide in methyl alcohol have shown that neither freshly cast rods of cadmium nor spongy cadmium deposited electrolytically are reproducible. Similarly, a reproducible *E.M.F.* is not obtained when freshly cast cadmium rods are used as electrodes in aqueous cadmium iodide solutions. Cadmium rods which have become grey by standing in cadmium iodide solution give a constant *E.M.F.* when measured against a non-polarisable electrode.

The behaviour of cadmium electrodes in concentration cells is considered to be due to allotropic change. Crystalline electrolytic deposits of cadmium on cadmium rods or platinum give a repro-

ducible *E.M.F.* when measured against a non-polarisable electrode, but this *E.M.F.* is slightly higher than that given by the grey cadmium electrodes. Amalgamated electrodes are not reproducible. It is shown by means of photomicrographs that a change takes place in the crystalline form which confirms the conclusions drawn from the *E.M.F.* measurements. Attempts to inoculate the surface of freshly cast cadmium with the stable modification have indicated that the action is extremely slow. The change is due in all cases to a deposit, and not to a pitting of the surface. E. G.

Application of Integral Equations to the Theory of Electrolysis. KURT SCHELLENBERG (*Ann. Physik*, 1915, [iv], **47**, 81—127).—A mathematical paper in which the properties of binary electrolytes are deduced by strict mathematical analysis on the basis of the molecular theory and Coulomb's law.

H. M. D.

Separations from Flames by Electricity and Experiments on the Validity of Faraday's Law in Flame Conduction. BRUNO THIEME (*Zeitsch. physikal. Chem.*, 1915, **89**, 693—727).—A continuation of the work previously published (A., 1912, ii, 123, 321). The present experiments are made with high-voltage direct current and low-voltage alternating current. It is shown that when a voltage of 455 is applied to two plates in a small luminous flame, a current flows of maximum value 0·0000025 ampere, thus indicating that the resistance of the flame is 182,000,000 ohms. It is also shown that the flame is broadened along the cathode when a potential difference exists between two plates inserted into a flame. If only the positive pole is placed in the flame, the flame is shortened slightly, whilst if the negative pole is placed in the flame it is slightly lengthened. The small columns of carbon which are deposited on the electrodes are shown to move in accordance with the laws governing the movement of an electric conductor through which a current is flowing when it is placed in a magnetic field. Quantitative measurements are made of the amount of carbon deposited at voltages varying from 123—449, and current strengths from 0·0008—0·0048 ampere, and it is shown that if the carbon is assumed to be univalent, the quantities deposited are in accordance with Faraday's law. Further experiments on the electrolytic deposition of copper from a flame fed with a solution of copper sulphate also point to the validity of Faraday's law in the case of deposition from flames. J. F. S.

Simple Quartz Mercury-vapour Lamps for Biological and Photochemical Investigations. W. T. BOVIE (*J. Biol. Chem.*, 1915, **20**, 315—320).—Directions are given for the preparation of several forms of mercury-vapour lamps from quartz tubing. For details, the original article must be consulted. H. W. B.

Correction of the Curie-Langevin Law of Magnetisation for the Mean Free Path of the Molecules. E. A. HOLM (*Ann. Physik*, 1915, [iv], **47**, 1—48).—The assumptions underlying

the deduction of the Curie-Langevin relation for paramagnetic substances are examined, and a correction factor introduced which depends on the mean free path of the molecules, the moments of inertia, and the mass of the molecules. The observed deviations from the simple law can be explained in terms of the modified formula. H. M. D.

Magnetochemistry of Manganous and Ferrous Salts. B. CABRERA, E. MOLES, and M. MARQUINA (*Anal. Fis. Quim.*, 1915, **13**, 256—270).—An account of an investigation of the magnetochemical properties of solutions of manganese chloride, sulphate, and nitrate, and of ferrous sulphate, carried out by Quincke's method. A. J. W.

Magnetic Manganese Alloys. XI. Manganese-Tin-Copper. FR. HEUSLER (*Zeitsch. anorg. Chem.*, 1914, **88**, 185—188. Compare Ross and Gray, A., 1911, ii, 183).—The maximum of magnetic properties is found, in accordance with the general rule, in the alloy in which the sum of the manganese and copper atoms is three times the number of tin atoms. In the aluminium series, the maximum is reached at $(AlMnCu_2)_x$. The ferromagnetic quality falls off much more rapidly from the maximum in the tin series than in the aluminium series. C. H. D.

Contractive and Expansive Volume- and Surface-Energy, Physico-chemical Properties and Thermal Condition of Matter: Frequency of Vibration of the Atoms in Elements and their Compounds and Mendeléev's Periodic Law. P. P. VON WEIMARN (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1905—1952).—This theoretical paper, in which the author gives more detailed consideration to the views previously advanced (A., 1913, ii, 753), consists essentially of a summary of arguments published in earlier papers. T. H. P.

Experimental Determination of the Critical Data for Oxygen, Nitrogen, Carbon Monoxide, and Methane. ETTORE CARDOSO (*Arch. Sci. phys. nat.*, 1915, [iv], **39**, 400—402).—The values obtained for the critical pressure and temperature are: nitrogen, 33·65 atm., −144·7°; carbon monoxide, 34·60, −138·7°; oxygen, 49·30, −118·0°; methane, 45·60, −82·85°. H. M. D.

Investigations on Ammonia. VI. The Specific Heat of Ammonia. F. HABER and S. TAMARU (*Zeitsch. Elektrochem.*, 1915, **21**, 228—241. Compare this vol., ii, 418, 419).—The specific heat of ammonia has been determined at three temperatures between 309° and 523° by two methods, which consist in passing the gas through a heater and then into a calorimeter, and determining the heat change. For details of the apparatus, the original must be consulted. Experiments have also been carried out with air, carbon dioxide, and hydrogen. The following values have been obtained for ammonia at constant pressure: 309°, 10·3 (10·2);

422°, 11·0 (11·0); and 523°, 11·8 (11·8), the bracketed values being those calculated from theoretical considerations by means of the formula $c_p = 8{\cdot}62 + 0{\cdot}0035t + 5{\cdot}1 \times 10^{-6}t^2$. The intramolecular energy of the ammonia molecule is calculated for various temperatures, and further calculations are made to show that the present experimental results are not opposed to the quantum theory. J. F. S.

Thermochemistry of Compounds of Copper and Aluminium. Luigi Rolla (*Gazzetta*, 1915, **45**, i, 192—196).—Determinations of the specific heats of various intermetallic compounds carried out by Schimpff (A., 1910, ii, 181) and by Schübel (A., 1914, ii, 530) seem to prove that deviations from Neumann and Kopp's law cannot be attributed to either the heat of formation or the position of the compound on the melting-point curve. Of these compounds, the author considers Cu_3Al, CuAl, and $CuAl_2$.

Making use of the relation established by Einstein, and generalised by Nernst, the specific heats may be calculated from Lindemann's formula, $\nu = 2{\cdot}8 \cdot 10^{12} \cdot \sqrt{T_f/mv^{\frac{2}{3}}}$ (1), which gives the atomic frequency of an element as a function of the absolute melting point, the atomic weight m, and the atomic volume v. In the case of a binary compound, $\nu'/\nu = \sqrt{T_f'/T_f} \cdot \sqrt[3]{v/v'}$ (2), where ν', T_f', and v' indicate, respectively, the frequency, absolute melting point, and atomic volume of the element in combination. For metallic solid solutions, with which it is assumed that the specific volume follows the law of mixtures, this reduces to $\nu'/\nu = \sqrt{T_f'/T_f}$, where T_f' denotes the absolute melting point of the alloy. In order to determine approximately the influence of the factor $\sqrt[3]{v/v'}$ of equation (2) in the case of copper–aluminium alloys, the author has measured the specific volumes of the three definite compounds. In each instance, the compound is formed with diminution in volume of the solid components, the percentage contractions being 2·9, 3·8, and 4·0 for CuAl, $CuAl_2$, and Cu_3Al respectively. The influence of the specific-volume factor of equation (2) is, therefore, not negligible, and the molecular heat cannot be calculated merely from the melting point. A quantitative solution of the problem is not possible, since the absolute value of the specific volume of each of the components in the alloy cannot be determined experimentally.

The heats of formation of the three compounds in Cal. per kilogram-mol. are found to be: CuAl, +32·38; $CuAl_2$, +23·29; Cu_3Al, −13·33. The most highly exothermic is, therefore, that formed with the least contraction, and there appears to be no relation between the heat of formation and the deviation from Neumann and Kopp's law. T. H. P.

Specific Heat and Heat of Fusion of Ice. H. C. Dickinson and N. S. Osborne (*J. Washington Acad. Sci.*, 1915, **5**, 338—340).—The measurements were made by means of an "aneroid calorimeter" in which equalisation of temperature is secured by the

high thermal conductivity of copper. From experiments with four samples of ice of varying degrees of purity, it has been found that the specific heat s in 20° calories at any temperature θ can be represented by the equation $s=0{\cdot}5057+0{\cdot}001863\theta-79{\cdot}75l/\theta^2$, in which l is the difference between 0° and the initial freezing temperature of the water from which the ice was obtained. The conclusion is drawn that the specific heat of pure ice may be represented by the equation $s=0{\cdot}5057+0{\cdot}001863\theta$.

The mean value obtained for the heat of fusion (in 20° calories) is 79·76. H. M. D.

Photoelectric Constant and Atomic Heat. T. Carlton Sutton (*Phil. Mag.*, 1915, [vi], **29**, 734—736).—The energy required to expel an electron from the atom with velocity v is kv, where k is the photoelectric constant. It is shown that the values of k for a number of metals do not differ very much from the value of the quantum ($6{\cdot}6\times10^{-27}$ erg.). In general, the k values, although invariably less than that of the quantum, are low when the atomic heat is high, and vice versa. With certain exceptions, the product of the photoelectric constant and the atomic heat is approximately equal to $35{\cdot}5\times10^{-27}$.

The interpretation suggested is that the proportion of absorbed quanta which influences the heat capacity is inversely proportional to the number of quanta which affect the photoelectric constant. H. M. D.

Re-calculation of Some Thermal Relations. W. Herz (*Zeitsch. anorg. Chem.*, 1914, **89**, 397—400).—The statement that the product of the absolute melting point of metals and the linear coefficient of expansion is a constant only holds good if the coefficient be measured near to the melting point. Aluminium, lead, cadmium, mercury, copper, platinum, and silver give values very near to 0·023, whilst tin and bismuth give much lower values. Iron, sodium, nickel, and palladium give normal values at sufficiently high temperatures.

The rule that the quantity, specific heat × absolute boiling point : atomic weight, shows simple relations within any periodic group is approximately fulfilled when the specific heat is taken at the ordinary temperature.

The relation that the molecular heat of volatilisation divided by the cube root of the molecular volume is a constant is also fulfilled at the boiling point, but the relation, absolute boiling point : square root of density = const., is not confirmed. C. H. D.

The Interpretation of Cooling Curves. H. Hanemann (*Zeitsch. anorg. Chem.*, 1914, **90**, 67—80. Compare Gulliver, A., 1914, ii, 623).—Geometrical methods of correcting the cooling curves of solid solutions are given, taking into account the relative quantities of heat developed at different stages of the cooling process. One conclusion is that when liquidus and solidus are approaching one another with falling temperature, the end of the

crystallisation is more clearly marked on the cooling curve than the beginning. The positions of certain curves in the accepted equilibrium diagrams of indium–thallium alloys, and the δ-iron region of the iron–carbon system, are criticised from this point of view. C. H. D.

Application of the Method of Heating to the Investigation of Binary Eutectic Systems: New Application of the Method, Principally to Systems Containing Silicates. N. I. BEZBORODKO (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1830—1874).—The application of the method of heating to the determination of temperatures of fusion (compare Flavicki, *ibid.*, 1896, **28**, 424; A., 1909, ii, 886) has been of limited extent in comparison with the method of cooling. The author has applied the method to the determination of the eutectic points of a number of binary systems already investigated by the cooling method by various authors.

The results show that a mechanical mixture of two compounds in the eutectic proportions, when heated comparatively rapidly, generally begins to melt at the eutectic temperature. The phenomenon of superheating often encountered is not to be regarded as unavoidable. In order to obtain fusion without superheating, such intimate mixture of the two components as is attained by preliminary fusion and slow crystallisation is unnecessary, careful mechanical mixture of the finely ground components being sufficient. The method is found to be applicable to the determination of the eutectic points of mixed salts, and also of mixed sulphides and silicates. It is especially suited to the investigation of: (1) substances which dissociate at high temperatures, such as (*a*) silicates, principally of the group of contact-metamorphic minerals, and other compounds unstable at high temperatures lower than their melting points; (*b*) silicates and other compounds unstable at their melting points, and separating into new components on solidification; (*c*) sulphides and other components dissociating, with evolution of gases, on heating. (2) Silicates exhibiting a tendency to form a glassy mass on solidification.

T. H. P.

The Cryoscopic Constant of Mercuric Iodide. ERNST BECKMANN, RUDOLF HANSLIAN, and MARIA MAXIM (*Zeitsch. anorg. Chem.*, 1914, **89**, 167—170. Compare Beckmann, A., 1907, ii, 739; Guinchant, *ibid.*, 667).—An electric furnace is used. The constant, extrapolated to infinite dilution, is 540, in agreement with that found by Guinchant, 550. This is confirmed by using α-bromonaphthalene vapour for heating. The molecule of mercurous iodide in solution is found to be Hg_2I_2. C. H. D.

Investigations with Phenylhydrazine. IV. Cryoscopic Measurements of the Capacity to Form Phenylhydrazones. BERNARDO ODDO (*Gazzetta*, 1915, **45**, i, 262—282).—Towards

phenylhydrazine as a cryoscopic solvent, hydrocarbons, alcohols, phenols, acids, and bases behave normally, or almost so, whereas aldehydes and ketones condense more or less readily with the solvent to form phenylhydrazones, the molecular weights obtained being, therefore, only one-half as great as the theoretical values (A., 1913, i, 1233). The experiments now described were made with the object of obtaining a comparative criterion for the aldehydic or ketonic function of a compound, the value of the molecular ratio, phenylhydrazine : carbonylic derivative, being kept approximately constant in the different cases, and the time factor of the reaction at a given temperature investigated. Curves are given showing, for each system, the relation between the freezing point and the time, these curves being continued to the point where the molecular weight of the carbonyl compound is one-half of the calculated value.

Small differences are found in the velocity of the reaction for members of a homologous series. In the series acetone, methyl propyl, methyl *iso*propyl, methyl butyl, methyl *iso*butyl, and methyl hexyl ketones, the time necessary for the completion of the condensation with phenylhydrazine increases gradually with increase in the number of methylene groups, the increase being sensibly the greater with the isomeride containing a branched chain.

Aromatic aldehydes react more readily than those of the aliphatic series, giving precipitates of the phenylhydrazones, and consequently the halved molecular weights almost immediately. Only in the case of piperonaldehyde is the reaction non-instantaneous, this being probably due to the presence of the methylenedioxy-group in the molecule. Both aliphatic and aromatic aldehydes react more readily than the corresponding ketones, but this is not the case with the *cyclo*hexanones, which approach the aromatic aldehydes in the rapidity of their action. T. H. P.

Investigations with Phenylhydrazine. V. Behaviour of Hemihydrated Phenylhydrazine as a Cryoscopic Solvent. Bernardo Oddo (*Gazzetta*, 1915, **45**, i, 283—292).—The results of the author's study of the equilibrium of the system phenylhydrazine–water (A., 1913, i, 1233) indicate the existence of the hemihydrate, $(NHPh\cdot NH_2)_2,H_2O$, but are not in agreement with Blanksma's statement that a second eutectic exists containing 4·6% of phenylhydrazine (A., 1910, ii, 594). The value previously obtained from measurements with diphenyl, naphthalene, and veratrole for the molecular depression of the hemihydrate, namely, 44·15, agrees well with that obtained with dibenzyl, 44·25; safrole, containing a methylenedioxy-group, gives 42·81. The number calculated by means of van't Hoff's formula is 40·28.

Cryoscopic measurements of a number of hydrocarbons, alcohols, phenols, acids, and bases in the hemihydrate have now been made. All the compounds examined exhibit normal behaviour comparable with that shown in anhydrous phenylhydrazine. With the hydro-

carbons, and, to a less extent, with the alcohols, the molecular weights increase gradually with the concentration. T. H. P.

Vapour Pressure of Iodine Between 50° and 95°. GREGORY PAUL BAXTER and MERRITT ROY GROSE (*J. Amer. Chem. Soc.*, 1915, **37**, 1061—1072).—Baxter, Hickey and Holmes (A., 1907, ii, 253) have determined the vapour pressure of solid iodine between 0° and 55° by passing a measured volume of dry air over pure iodine, and then into a solution of sodium sulphite. The iodine absorbed by the sulphite was estimated by precipitating it as silver iodide. The method has now been extended to the determination of the vapour pressures at temperatures up to 95°.

It was found that at these higher temperatures sodium sulphite could not be used to absorb the iodine, as it is too easily oxidised by the oxygen of the air current at such temperatures. The air, after being passed over the iodine, was therefore led into a solution of sodium carbonate. The solution was afterwards acidified, the liberated iodine reduced by means of hydrazine, and the iodine precipitated as silver iodide.

From the results of these experiments, the following average values for the vapour pressure were obtained: at 50°, 2·154 mm.; at 55°, 3·069; at 60°, 4·285; at 65°, 5·962; at 70°, 8·196; at 75°, 11·21; at 80°, 15·09; at 85°, 20·21; at 90°, 26·78; at 95°, 35·24 mm.

These results, and those of Baxter, Hickey and Holmes (*loc. cit.*), may be expressed by either of the two formulæ:

$$\log p = -106{\cdot}3930 + 46{\cdot}611 \log T - 0{\cdot}031677T$$

and $\log p = 9{\cdot}7522 - 2863{\cdot}54/(T - 19)$.

The average molecular heat of sublimation of solid iodine between 50° and 95° has been calculated by means of the Clausius equation, and found to be 14·7 kilogram calories, or 61·6 kilojoules. E. G.

Entropy of Vaporisation as a means of Distinguishing Normal Liquids. JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1915, **37**, 970—978).—It has been found from a consideration of existing data that the entropy of vaporisation, that is, the molecular heat of vaporisation divided by the absolute temperature at which vaporisation takes place, is the same for all normal liquids when the vaporisation takes place at the same concentration of vapour, and not, as in Trouton's rule, when it takes place at the same pressure (one atmosphere). This fact can be expressed in the form of a vapour-pressure equation containing a single constant characteristic of the liquid, this constant being determined from the temperature necessary to give the same concentration of vapour in the different cases. E. G.

Fractional Distillation with Regulated Still-heads. II. Distillation of Ternary Mixtures. M. A. ROSANOFF, JOHN F. W. SCHULZE, and R. A. DUNPHY (*J. Amer. Chem. Soc.*, 1915, **37**, 1072—1079).—Rosanoff and Bacon (this vol., ii, 84) have

studied Brown's law relating to the distillation of mixtures through a regulated still-head, and have made experiments on the distillation of binary mixtures with a still-head maintained at a constant temperature. It was found that in the case of mixtures in which the b. p. curve passes through a maximum or a minimum, two different distillates may be expected at certain temperatures, depending on the composition of the liquid originally introduced into the still, but that whichever of the two possible distillates is produced, the distillation proceeds in conformity with Brown's law, in so far as the composition of the distillate is constant and is identical with that of the vapour evolved by a mixture, the b. p. of which is equal to the temperature of the still-head.

Experiments have now been made with ternary mixtures of toluene, carbon tetrachloride, and ethylene dibromide, the still-head being maintained at temperatures of 83°, 91°, 99°, 107°, and 115°. It was found that the variation of the distillate during a single distillation was comparatively slight, and that practically the regulated still-head can be used to obtain a uniform distillate from such mixtures, as well as from simple binary mixtures.

In general, when the number of substances in the mixture is three or more, the composition of the distillate depends not only on that of the original mixture, but varies in the course of a single distillation. This variation, however, is moderate, and the nearer the constant temperature of the still-head is to the b. p. of the most volatile component, the more nearly constant is the composition of the distillate. E. G.

Solutions of Metals in Boiling Mercury. Ernst Beckmann and Otto Liesche (*Zeitsch. anorg. Chem.*, 1914, **89**, 171—190).—In order to prevent bumping in boiling mercury, vigorous stirring must be used. The glass apparatus contains 200 grams of mercury, and is heated in a bath of molten tin. An atmosphere of dry carbon dioxide is used. A stoppered tube provided with taps for the passage of dry carbon dioxide is described for weighing the alkali metals.

The ebullioscopic constant of mercury is 114·0. The metals of the alkalis and alkaline earths, together with thallium, give results indicating the existence of compounds in the liquid amalgams. An approximate calculation points to the formulæ $NaHg_5$ or $NaHg_6$, KHg_{12} or KHg_{14}, and $CaHg_{10}$. Gold, silver, cadmium, and zinc dissolve in the monatomic form without combination, whilst lead, tin, and bismuth show slight association (compare Smith, this vol., ii, 89, 319). C. H. D.

Metastability of the Metals in Consequence of Allotropy and its Significance for Chemistry, Physics, and Technics. IV. Ernst Cohen and W. D. Helderman (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1238—1241. Compare this vol., ii, 83).—The fact that many metals consist of mixtures of allotropic modifications in varying proportions will have considerable influence on the thermochemical data for the reactions in which

these metals are involved. The heats of reaction recorded in the literature must be considered as fortuitous values depending on the previous history of the metals concerned. The same applies to the latent heat of fusion, and by reference to the recorded values it is found that these show differences amounting to 20% for lead and to 80% for sodium. These data must be redetermined by observations on definite allotropic forms of the metal.

H. M. D.

Thermochemical Significance of the Coefficient "*i*" (of *PV*=*iRT*). A. Bogorodski (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1716—1734).—The author has previously (A., 1905, ii, 711) advanced the paradoxical theorem that the thermal relations of salts, anhydrides, bases, and water give reason for regarding the dissolution of a salt as a hydrolytic action of a special type. This view, of which Mendeléev discussed the possibility ("Principles of Chemistry," 1905, I, 86, 355), is now subjected to more detailed consideration. The resultant conclusion is that, on dissolution, a salt, *MR*, is transformed into systems of the general types $M(OH)_n(H_2O)_x$ and $RH_n(H_2O)_y$, these complexes occurring partly in mutual combination, forming the undissociated portion of the salt, and partly in equilibrium with one another and with the solvent. To the complexes in the latter condition are attributed those properties which, according to the view generally accepted, are due to the ions. In the light of this interpretation, the heat of neutralisation would be the heat of formation of the hydrolysed, non-dissociated part of the salt. This being so, the cycle of thermal effects exhibited on formation of a salt may be expressed otherwise than is the case on the ionic hypothesis. If C_1 represents the heat of formation of a gram-molecule in solution, that is, in the completely hydrolysed condition, and C_2 the heat of formation of the dissociated part, so that C_2 is equal to C_1 less the heat of neutralisation, then the ratio $C_2 : C_1$ will have the same significance as the ratio of the osmotic pressures, $P_1 : P$, or of the electrical conductivities, $\Delta_\mu : \Delta_\infty$. This represents the coefficient of dissociation, and, therefore, van't Hoff's coefficient, *i*. With twenty-eight different salts, the ratio between the values of *i* determined thermally and cryoscopically lies within the limits 1·0 and 1·1, and in twenty-two cases between 1·00 and 1·05. Such agreement is difficult to regard as accidental.

T. H. P.

Investigations on Ammonia. IV. Determination of the Heat of Formation of Ammonia at High Temperatures. F. Haber and S. Tamaru (*Zeitsch. Elektrochem.*, 1915, **21**, 191—206. Compare *ibid.*, 89, 128; this vol., ii, 226).—The heat of formation of ammonia has been determined at a series of high temperatures. The method consists in leading a continuous stream of ammonia, heated to the required temperature, through a vessel containing a contact substance placed in a calorimeter. The heat used up in the decomposition is supplied electrically to the contact substance, and this quantity of heat represents the heat of formation

of the ammonia decomposed in the calorimeter. The quantity of ammonia decomposed is determined by a measurement of the volume of hydrogen and nitrogen passing from the calorimeter. The apparatus, which is fairly complicated, is described fully, together with a diagram, in the paper. Experiments were carried out at four temperatures, and the results calculated so as to give a lower and a higher limit to the value of the heat of formation; the various results agree among themselves, giving a difference of about 400 cal. between the two. The most probable values at the different temperatures in gram-calories per molecule are: 554°, 12,860; 659°, 13,100; 503°, 12,700; and 466°, 12,670.

J. F. S.

Investigations on Ammonia. V. Heat of Formation of Ammonia at Ordinary Temperatures. F. Haber, S. Tamaru and L. W. Oeholm (*Zeitsch. Elektrochem.*, 1915, **21**, 206—282. Compare preceding abstract).—The heat of formation of ammonia has been determined by leading ammonia at ordinary temperature through a vessel filled with a catalyst (osmium or iron), and placed in a calorimeter. A portion of the ammonia was decomposed, and the gases led away from the calorimeter at the same temperature as that at which they entered. The heat required for the decomposition is furnished to the catalyst by electrical means, and represents the heat of formation of that amount of ammonia which has been decomposed. The experiments are carried out differentially; first, the experiment is carried out with ammonia, and then, to guard against loss of heat from the calorimeter, it is repeated with a mixture of three volumes of hydrogen and one volume of nitrogen. A small amount of ammonia is formed in the latter case, but its quantity is shown to be so small that it can be neglected. A long account of the necessary precautions and details of the method of work and apparatus is given. It is shown that the heat of formation, at constant pressure, of ammonia at 0° lies between 10,950—11,000 gram-calories per mol. J. F. S.

The Heat of Formation of Vanadium Pentoxide and the Vanadium Chlorides. Otto Ruff and Lothar Friedrich (*Zeitsch. anorg. Chem.*, 1914, **89**, 279—306).—Vanadium containing 94% of the metal, the remainder being aluminium and alumina, is burnt with oxygen in a Berthelot bomb with the aid of sodium peroxide, the salt formation being allowed for by separate experiments. The results give the heat of formation of V_2O_5 as 437±7 Cal. (compare Mixter, A., 1912, ii, 899). Vanadium trioxide may also be burnt with sulphur and sodium peroxide. Its heat of formation is 302±10 Cal. The heat of solution of pure vanadium pentoxide in a solution of sodium hydroxide and peroxide has also been determined, the same alkaline solution then being used to dissolve the chlorides. A closed form of calorimeter is used, allowing gradual mixing. The following values are obtained for the heats of formation: $VOCl_3$, 200±4 Cal.; VCl_2, 147±4 Cal.; VCl_3, 187±8 Cal.; VCl_4, 165±4 Cal. The dichloride

is oxidised in a Berthelot bomb, pentoxide, oxychloride, and chlorine being obtained, so that an analysis of the product is required for the calculation. The trichloride, prepared by the action of sulphur on a mixture of tetrachloride and oxychloride, has not been obtained pure, and a correction is made for the sulphur content. Combustion in the bomb gives better results than the solution method.

A calculation gives about 630° as the lower limit of stability of vanadium tetrachloride. C. H. D.

New Form of Adiabatic Calorimeter. V. Sventoslavski and I. Pakovitsch (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1284—1293).—The authors describe in detail the construction of a new type of adiabatic calorimeter, and discuss the accuracy necessary in adjusting the temperatures of the liquids in the jackets surrounding the calorimetric chamber (compare Richards and Burgess, A., 1910, ii, 391; Benedict and Higgins, *ibid.*). T. H. P.

Adiabatic Determination of the Heat of Combustion of Benzoic Acid. V. Sventoslavski, M. Popov, and I. Pakovitsch (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1293—1301).—The results of the measurements here given show that adiabatic, calorimetric determinations are possible by means of the calorimeter devised by Sventoslavski and Pakovitsch (preceding abstract). The curves showing the rise of temperature of the calorimetric vessel and of its envelope are practically superposable, the slight divergences extending over such short periods of time that no appreciable radiation from the calorimeter occurs. The heat of combustion of 1 gram (abs.) of benzoic acid at constant volume is found to be 6304·6 cal. at 17°, this value being 0·9% less than that obtained by non-adiabatic measurements.

T. H. P.

Regnault-Pfaundler Formula. V. Sventoslavski (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1302—1310).—Further experiments (compare preceding abstracts) show that the results of adiabatic differ from those of non-adiabatic measurements, the heat effects in the former case being 0·1% less than in the latter. The Regnault-Pfaundler formula gives accurately the loss of heat due to radiation, but inaccurately that due to evaporation of water from its surface, non-adiabatic measurements in which the influence of evaporation of water is removed being in good agreement with the adiabatic determinations. These results were obtained from calorimetric measurements of the heat of combustion of benzoic acid in a Berthelot bomb, and the velocity with which this process takes place, and the rise of temperature curve, are not typical of all heat processes. Since, however, in certain cases the Regnault-Pfaundler formula is inapplicable to the calculation of the loss of heat from the calorimeter, it is essential that calorimetric measurements of natural constants, such as the mechanical equivalent of heat and the specific heat of water, should be made under condi-

tions that exclude the possibility of an error in the radiation correction. T. H. P.

Heats of Combustion of Aromatic Hydrocarbons and *cyclo*-Hexane. THEODORE W. RICHARDS and FREDERICK BARRY (*J. Amer. Chem. Soc.*, 1915, **37**, 993—1020).—The adiabatic method of calorimetry has been further improved with special reference to its employment for the determination of heats of combustion in the Berthelot bomb, and has been found capable of yielding very concordant results. The relative heats of combustion of sucrose and several hydrocarbons have been determined.

Regarding the heat of combustion of sucrose as 16·498 kilojoules per gram, the absolute heats of combustion of 1 gram of the following substances, expressed in kilojoules and determined at 18°, have been found to have the values: benzene, 41·79; toluene, 42·51; ethylbenzene, 42·96; mesitylene, 43·24; *n*-propylbenzene, 43·34; *iso*propylbenzene, 43·37; ψ-cumene, 43·14; *tert.*-butylbenzene, 43·60; *cyclo*hexane, 46·69. These results, and those of Richards and Jesse (A., 1910, ii, 269), show a striking similarity between the heats of combustion of isomerides.

Pure toluene has b. p. 110·31°, and *cyclo*hexane, b. p. 80·8°. Benzene and *cyclo*hexane have m. p.'s 5·484° and 5·97° respectively. E. G.

Densities of the Coexisting Phases of Methane and Carbon Monoxide. ETTORE CARDOSO (*Arch. Sci. phys. nat.*, 1915, [iv], **39**, 403—404).—The orthobaric densities of methane and carbon monoxide have been measured over a considerable range of temperature. The critical density of methane is 0·1623, and of carbon monoxide 0·3110. H. M. D.

The Volume Surfaces of Liquid Benzene and Phenol and of Solid Benzene, Naphthalene, and Sodium Chloride. HARRY ESSEX (*Zeitsch. anorg. Chem.*, 1914, **88**, 189—233).—Glass piezometers are used, water, oil, or mercury being used as a filling liquid. The change in level is measured by means of a narrow tube containing mercury, down the middle of which a thin platinum wire is stretched. The resistance of the exposed portion of the wire is determined. The whole apparatus is enclosed in a steel bomb with castor oil, immersed in a thermostat. Measurements have been carried up to 3000 kg./cm.^{2}

Five volume isotherms for liquid benzene have been determined, at 20°, 40°, 60°, 80°, and 100°, and eight for liquid phenol, at intervals of 10° from 50° to 120°. Of solid substances, the volume isotherms of benzene have been determined at 0°, 20°, and 40°; of naphthalene at 20°, 40°, 60°, 80°, and 100°; and of sodium chloride at 0°, 20°, 50°, and 80°.

The variations with pressure of the work done in compression, heat of compression, specific heat, and internal energy have been calculated for liquid phenol and solid benzene, naphthalene, and sodium chloride. Those portions of the volume surface of liquid

benzene and phenol which adjoin the melting curve have been compared with the surfaces calculated from Tammann's equation of condition, a satisfactory agreement being found.

Liquid phenol exhibits certain abnormalities in the variation of the thermal expansibility with temperature, and of the compressibility with pressure, the coefficient of the former passing through a maximum and that of the latter through a minimum. The effect is due to the formation of the second crystalline modification, phenol II. Molecular-weight calculations by Tammann's method give $(C_6H_5\cdot OH)_2$ for both phenol I and II, but indicate a simple molecule, which is present in greater quantity as the temperature rises, and may crystallise at high pressures.

The volume surfaces of the three solids examined all show volume isotherms which are convex to the axis of pressure, and flatten at higher pressures and lower temperatures. The volume isobars are slightly convex to the axis of temperature, whilst the isometric lines are nearly rectilinear, being parallel for anisotropic substances, but converging towards the absolute temperature for isotropic substances. C. H. D.

Organic Liquids and Alkaline Solutions. T. J. Twomey (*J. Physical Chem.*, 1915, **19**, 360—362).—It is shown that organic liquids, such as chloroform, carbon tetrachloride, and benzene, when dropped into water or acid, form spherical drops, whereas when dropped into solutions of alkalis they form flattened drops, which are much less mobile than the drops in the former case. When the drops are formed in an alkaline solution, they regain the spherical shape on the solution being made acid. Similar results were obtained in the case of a solution of potassium cyanide. The flattening in alkaline solution is stated to be due to adsorption. J. F. S.

The Relation between Viscosity and Chemical Constitution. IX. The Viscosity and Fluidity of the Aliphatic Acids. Albert Ernest Dunstan (T., 1915, **107**, 667—672).—According to previous results (T., 1913, **103**, 127; 1914, **105**, 782), homologous series of compounds show a linear relation between the logarithm of the viscosity and the molecular weight. Measurements have now been made of the viscosity of the aliphatic acids at a number of different temperatures. At one and the same temperature, the values of the homologous increment of the logarithm of the viscosity are said to be roughly constant between propionic and nonoic acids. For the higher acids, the increment decreases considerably with the number of carbon atoms. Formic and acetic acids have abnormally high viscosities. H. M. D.

The Viscosity of Aqueous Solutions of Potassium Haloids. Charles A. Kraus (*Zeitsch. anorg. Chem.*, 1914, **88**, 171—172. Compare Hertz, A., 1914, ii, 344).—The observation that the viscosity of many solutions of alkali haloids is less than that of pure water was made by Sprung (*Ann. Phys. Chem.*, 1876,

[ii], **159**, 1), whose measurements cover a large number of salts from 0° to 60°, but have been generally overlooked. Sprung found that the viscosity of solutions of ammonium chloride, bromide, and nitrate, potassium chloride, bromide, iodide, and chlorate, and sodium iodide passed through a minimum which was lower than that of pure water, provided that the temperature was low. With increasing temperature, the minimum became less pronounced, and ultimately disappeared. C. H. D.

The Viscosity of Salt Solutions. W. Herz (*Zeitsch. anorg. Chem.*, 1914, **89**, 393—396). Compare Kraus, preceding abstract).—The viscosity curves of the sulphates, chlorides, and nitrates of the divalent metals examined all have the same form, and the sulphates of copper, magnesium, zinc, and manganese give practically identical curves. A comparison of the nitrates and sulphates shows that the viscosity increases with the atomic weight of the metal. C. H. D.

Viscosities of Binary Mixtures of the Associated Liquids, Water, Formic Acid, and Acetic Acid. P. B. Davis and Harry C. Jones (*J. Amer. Chem. Soc.*, 1915, **37**, 1194—1198).—Jones and Murray (A., 1903, ii, 637) have shown that when two associated liquids are mixed, each diminishes the association of the other. Jones and Veazey (A., 1907, ii, 438; 1908, ii, 259, 260) have suggested that the increase in viscosity which results in such cases is due to the larger number of smaller molecules which are present, and the consequent increase of friction, viscosity being a function of the surface friction of molecules.

The viscosities of binary mixtures of water, formic acid, and acetic acid have been determined at 15° and 25°, and curves have been constructed by plotting the viscosities against the concentrations. The results show that the viscosities of acetic acid in water pass through a well-defined maximum, those of formic acid in acetic acid pass through a slight maximum, whilst those of water and formic acid fall almost on a straight line. These results are in harmony with Jones and Veazey's suggestion, which has been already mentioned, and also with their explanation of the cause of the lowering of the viscosity of water and other solvents by salts, the cations of which have very large ionic volumes, such as those of potassium, rubidium, and cæsium (*loc. cit.*). E. G.

Internal Friction of the System Aniline–Allylthiocarbimide. N. Kurnakov and I. Kviat (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1372—1388).—The viscosity diagrams of the binary system aniline–allylthiocarbimide are of the rational type (compare Kurnakov and Shemtschushni, A., 1913, ii, 190), and exhibit singular or Dalton points corresponding with equal molecular proportions of the components, that is, with the formation of phenylallylthiocarbamide, this compound crystallising out when the liquid mixtures are cooled below 98·5°. The maximum temperature of the

melting-point curve also corresponds with equimolecular proportions of the constituents. The composition at the singular points remains unchanged under the influence of the factors of the equilibrium, namely, the temperature and the concentration of a third substance. The general characters of the composition-property diagrams are similar for all properties of the system.

T. H. P.

The Adsorptive Power of the Hydroxides of Silicon, Aluminium, and Iron. VII. PAUL ROHLAND (*Zeitsch. anorg. Chem.*, 1914, **89**, 164—166. Compare A., 1913, ii, 302).—Complex dyes are adsorbed by the colloids of clay if of a colloidal character, but not if crystalloid. The adsorption may be made a means of distinguishing between these conditions. A dye may pass from the one class to the other with changing dilution. C. H. D.

Neutralisation of Adsorbed Ions. WILDER D. BANCROFT (*J. Physical Chem.*, 1915, **19**, 363—376).—A theoretical paper in which it is shown that the neutralisation of an adsorbed ion is due to specific adsorption. The concentration of a given electrolyte necessary to neutralise the charge on a given colloid will therefore depend on the nature of both ions and on the nature of the colloid. It is inaccurate to state that the cation is negligible in the precipitation of a positive colloid, and the anion in the precipitation of a negative colloid, although this statement is often approximately true. Ions of the same valency are not all adsorbed alike. The order of adsorption is specific with each colloid, and is not determined exclusively, probably not at all, by the migration velocity or solution pressure of the ion. Since the adsorption is specific, Schulze's law is only an approximation. Some univalent ions are adsorbed by certain colloids more than some divalent or tervalent ions. In many cases there is, however, a marked tendency to increased adsorption with increasing valency. Mixtures of two sols will not precipitate each other unless adsorption takes place. Since adsorption is specific, the order of precipitation of a negative sol by a number of positive sols will not necessarily be the same for any two negative sols. Adsorption often takes place between two similarly charged sols; the statement that similarly charged sols have no action on one another is therefore inaccurate. Hydrated chromic oxide, which is peptonised by potassium hydroxide, may act as a protecting colloid for hydrated ferric oxide, which is not peptonised by potassium hydroxide. Since an adsorbed ion does not necessarily give the reactions of a free ion, electrometric measurements may lead to false conclusions when applied to colloidal solutions, and in this connexion it appears probable that sodium palmitate is hydrolysed to a much greater extent in solution than appears from electrometric measurements. If two colloidal sols did not adsorb each other appreciably, and if one adsorbed the cation of a given electrolyte very markedly, whilst the other adsorbed the anion to a similar extent, the addition of such an electrolyte in small quantity to such a mixture of sols

would produce a solution which would conduct electricity without there being any appreciable amount of substance in true solution. In sodium palmitate solutions, it seems probable that the hydroxyl ions set free by hydrolysis are adsorbed practically completely by the colloidal soap. Addition of a colloid to a solution will increase or decrease the conductivity if the adsorbed ion has a greater or less migration velocity than the ion not adsorbed. When adsorption by a colloid causes hydrolysis, the conductivity will depend also on the nature of the products of hydrolysis. J. F. S.

A Vacuum Furnace for the Measurement of Small Dissociation Pressures. R. B. SOSMAN and J. C. HOSTETTER (*J. Washington Acad. Sci.*, 1915, **5**, 277—283).—An electrical furnace is described for use in the determination of very small dissociation pressures. The furnace consists of a tube of a rhodium–platinum alloy containing 20% of rhodium. The furnace walls themselves are directly heated by the passage of a low voltage alternating current. The furnace is surrounded by a water-cooled jacket, which can be exhausted, so that during a measurement the furnace is in a vacuum, and consequently there is no danger of the walls collapsing, or, indeed, of changes of volume occurring which will influence the pressure inside the furnace. A rhodium–platinum thermoelement, and an arrangement for external optical temperature measurements, are provided, as well as three pumps with the necessary pressure gauges. Pressures between 2·5 atms. and 0·000001 mm. can be registered, and temperatures up to 1450° obtained. The efficiency of the furnace compares favourably with that of other types of electric furnaces; thus, a current of 580 amperes at 1·8 volts gives a temperature of 1450°, which is constant to about 1°. J. F. S.

The Kinetic Interpretation of the Osmotic Pressure. P. EHRENFEST (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1241—1245).—A theoretical paper, in which the author, by making use of Clausius' virial hypothesis, shows that the osmotic pressure produced by collision of the molecules of solute against a semi-permeable membrane is correctly expressed by the gas equation $PV=RT$, provided that the solution is sufficiently dilute. H. M. D.

A Collodion Diffusion Cell for Use in Dialysis. T. R. BRIGGS (*J. Physical Chem.*, 1915, **19**, 377—380).—The author has prepared diffusion cells by coating the interior of Soxhlet extraction thimbles with a collodion solution containing quantities of glycerol up to 60%. These cells may be completely dried and kept for any length of time without losing their efficacy. From trial experiments, it is shown that cells prepared in this way are more efficient than ordinary parchment cells, but slightly slower in action than collodion sacs prepared by Novy's method. It is also shown that the permeability of the cells by water and salts increases with the percentage of glycerol added to the collodion solution up to 50%, after which it remains constant. J. F. S.

Condition of Carbonic Acid in the Blood. II. Mobility of the Ion, HCO_3', at 18°. E. D'AGOSTINO and G. QUAGLIARIELLO (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 638—645. Compare A., 1914, ii, 676).—The value of μ_∞ for solutions of sodium hydrogen carbonate in pure water is found, after a special correction is applied to eliminate the influence of hydrolysis, to be 84·4 at 18°. The corresponding mobility of the ion HCO_3' at 18° is, therefore, $84·4 - 43·6 = 40·8$, which is somewhat lower than the value, 41·4, obtained by Walker and Cormack (T., 1900, **77**, 5), who made no correction for hydrolysis. It was noticed that the conductivity of a solution of sodium hydrogen carbonate tends to increase slightly, presumably owing to liberation of carbon dioxide resulting from exposure of the solution to the air. That the increase of the sodium hydroxide thus caused may have an effect on the results of the measurements greater than that produced by hydrolysis is shown by further determinations of the conductivity, using (1) solutions of sodium and potassium hydrogen carbonates in carbon dioxide solution, and (2) solutions of sodium and potassium hydroxides in water containing excess of carbon dioxide in solution; the latter method appears to be the better for obtaining pure solutions of known concentrations. In this way, the mobility of the ion HCO_3' at 18° is found to have the value 39·3.

T. H. P.

Condition of Carbonic Acid in the Blood. III. Mobility of the Ion, HCO_3', at 37°. G. QUAGLIARIELLO and E. D'AGOSTINO (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 772—773. Compare preceding abstract).—The value of μ_∞ for sodium hydrogen carbonate at 37° is found to be 122·0, the corresponding mobility of the ion HCO_3' being $122·0 - 63·8 = 58·2$. T. H. P.

[Influence of Electrolytes on Solubility.] ERIK G. THORIN (*Zeitsch. physikal. Chem.*, 1915, **89**, 685—692).—The influence of a number of sodium salts on the solubility of ethyl ether in water at 28° has been determined. The experiments were carried out by placing 100 c.c. of a $N/2$-solution of the salt in a flask and adding 5 c.c. of ether, and measuring the length of the column of ether formed in the narrow neck of the flask. The mixture was then shaken at 28°, and, after an hour, the undissolved column of ether again measured and the solubility calculated. The following values were obtained for the solubility of ether in 100 c.c. at 28°: water, 5·85 grams; $N/2$-solutions of sodium iodide, 5·70; sodium bromide, 4·68; sodium chloride, 4·48; sodium fluoride, 4·15; sodium sulphate, 4·30; sodium chromate, 4·22; sodium molybdate, 4·39; sodium tungstate, 4·12; sodium phosphate, 4·17; sodium arsenate, 4·20. It will thus be seen that the lowering of the solubility of ether increases with decreasing atomic weight of the characteristic element of the anion for each group of the periodic system, molybdenum, however, being an exception. A number of sodium salts of aliphatic and aromatic acids were also used, and it is shown that the salts of aliphatic acids reduce the

solubility in the same way as inorganic salts, whereas the salts of aromatic acids increase the solubility. A further series of experiments, on the influence of lithium chloride, calcium chloride, sodium iodide, and sodium bromide in various concentrations on the solubility of phenylthiocarbamide in absolute alcohol solution was also made. It is shown that 1000 c.c. of saturated alcohol solution contain 0·2065 gram-molecules of phenylthiocarbamide at 28°. The salts examined all increase the solubility, lithium chloride most strongly, and calcium chloride least strongly. The increase in solubility increases with the concentration of the dissolved electrolyte. J. F. S.

Topic Parameters and Morphotropic Relationships. WILLIAM BARLOW and WILLIAM JACKSON POPE (*Phil. Mag.*, 1915, [vi], **29**, 745—749).—From a consideration of the morphotropic relations exhibited by ammonium iodide and its tetramethyl, tetraethyl, and tetrapropyl derivatives, it is shown that topic parameters, as hitherto applied to the quantitative description of morphotropy (compare Slavik, A., 1902, ii, 561), are devoid of physical significance. A better view of the morphotropic relationships for a series of related compounds is obtained by consideration of the axial ratios and the crystal systems to which these belong. H. M. D.

The Molecular Structure of Solid Isotropic and Anisotropic Binary Mixtures. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1914, **90**, 297—326).—The two kinds of molecules in a binary mixture are quite irregularly distributed in an isotropic substance, but arranged more or less evenly in a space-lattice in an anisotropic substance. The solubility of the one component is diminished by the protective action of the other. In an isotropic mixture, the protective action may be calculated from the probability of a molecule being associated with any number of molecules of the second kind.

The solubility of glasses prepared by melting boron trioxide with silica has been tested, using boiling water and methyl alcoholic hydrogen chloride as solvents. The results do not show good agreement with theory, but adsorption has to be allowed for, and it is considered that the agreement is sufficient, and that the molecular weights of boron trioxide and silica in glasses are in the ratio of those indicated by their formulæ.

In a binary crystalline solid solution, the two kinds of molecules may either be distributed at random or regularly throughout the space-lattice. The results on extracting one component by means of a solvent should be quite different in the two cases.

A binary "mixed crystal" may depart from homogeneity in two ways, by zonal arrangement of the components, as in rapidly cooling from the fused state, and by irregular distribution in the space-lattice. The latter is probably more slowly remedied by annealing than the former.

The case of a cubic crystal is taken, the assumptions being made

that the distribution of *A*- and *B*-molecules is regular, and that the removal of *A* by a solvent does not alter the *B*-space-lattice. It has further to be assumed that the solvent acts very much more rapidly along the cubic edges than along the diagonals. The case is tested by parting alloys of gold and silver with nitric acid. The alloys are used in the form of thin plates $40 \times 20 \times 0{\cdot}1$ mm. Hard-rolled alloys dissolve more quickly than after annealing. The longer the annealing, the more regular the distribution in the crystal must become. Alloys containing more than 62·5 atomic % of silver part with practically the whole of their silver to nitric acid, whilst those which contain less than 50 atomic % are almost unattacked. The observed curve does not differ greatly from the theoretical. Alloys of gold and copper give similar results. C. H. D.

The Inoculating Effect of Isomorphous Substances. MEINHARD HASSELBLATT (*Zeitsch. anorg. Chem.*, 1914, **89**, 53—70).—Parallel growths of crystals on unrelated substances, such as that of potassium iodide on mica, are not to be regarded as effects of inoculation. Only zonal deposition is evidence of a certain degree of isomorphism between the inoculating substance and the undercooled substance. It is shown by reasoning from the thermodynamical potential that the inoculating crystal must be capable of forming solid solutions in all proportions with the undercooled substance. This has been tested for the following pairs, the liquidus curves of which lie between the freezing points of their components: $Cd(NO_3)_2,4H_2O$–$Ca(NO_3)_2,4H_2O$ (unstable modification), stilbene–azobenzene, stilbene–dibenzyl, and stilbene–benzylideneaniline.

When the liquidus presents a minimum, inoculation can only produce crystallisation when the temperature is below that of the minimum. This is confirmed for the systems azobenzene–dibenzyl, *m*-iodonitrobenzene–*m*-bromonitrobenzene, and *m*-iodonitrobenzene–*m*-chloronitrobenzene. Occasionally, crystallisation is found to occur slightly above the minimum, owing to partial solution of the inoculating crystal, and consequent cooling.

When two substances have identical space-lattices, but show a gap in the miscibility in the solid state, inoculation does not occur, even below the eutectic temperature. This is the case in the pairs azobenzene–benzylaniline, azobenzene–benzylideneaniline, benzylideneaniline–benzylaniline, stilbene–benzylaniline, and dibenzyl–benzylaniline. The test is a sensitive one for a gap in miscibility. Thus, stilbene brings about crystallisation in either undercooled azobenzene or benzylideneaniline, but these two substances, being only partly miscible in the solid state, are without effect on one another.

The *m*-halogen derivatives of benzene, when tested in this manner, prove to be completely isomorphous, with the exception of the pair *m*-fluorobenzene–*m*-iodobenzene, the chemical similarity here being least. *m*-Dinitrobenzene and *m*-nitrobenzonitrile are without effect on *m*-chloronitrobenzene.

In cases of incomplete miscibility, it is possible that inoculation might take place at very low temperatures, the gap of miscibility becoming less, but it has not been found possible to realise this case experimentally. C. H. D.

A Method for Distinguishing Tautomeric, Isomeric, and Polymeric from Polymorphic Substances. NEVIL VINCENT SIDGWICK (T., 1915, **107**, 672—678).—The method recommended is to add the less soluble form *B* to a saturated solution of the more soluble form *A* at constant temperature. If the two forms are polymorphic and give the same molecules in solution, *B* will not dissolve, but, on the contrary, some of the dissolved substance will separate out. If, on the other hand, the two forms are tautomeric, then *B* will dissolve, irrespective of the presence of *A*, provided that the tautomeric change of *A* into *B* is not too rapid. Tautomeric substances with a very high velocity of change in solution will, however, appear to be polymorphic.

The method has been applied to a number of substances, the changes in concentration being followed by determination of the freezing point of the solution. Benzene was used as solvent. Phthalylphenylhydrazide occurs in three forms: *A*, bright yellow (m. p. 184°); *B*, pale yellow (m. p. 184°); *C*, white (m. p. 216°). The test shows that *A* and *B* are polymorphic, whilst *C* is isomeric or tautomeric with them.

The white (m. p. 127°) and yellow (m. p. 127°) forms of phthalylphenylmethylhydrazide are polymorphic. The same result was obtained with needle and prismatic forms of *p*-bromoacetanilide and 2:4-dibromoacetanilide, and also with the two forms of *p*-nitrophenol.

The white and yellow forms of phthalylhydroxylamine (m. p. 220—226°) are probably tautomeric, and this was also found to be the case for the *A* (m. p. 114—117°) and *B* (m. p. 136—140°) forms of phenylglyoxalphenylhydrazone.

The *A* (m. p. 150°) and *B* (m. p. 128°) forms of methylcryptopine are polymorphic, whilst the *C* (m. p. 110°) form is isomeric or tautomeric with *A*. H. M. D.

Causes and Conditions of the Decolorisation of Colloidal Solutions of Arsenious Sulphide. N. P. PESKOV (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1619—1645).—Vorländer and Haberle (A., 1913, ii, 570) found that, in very dilute solution, arsenious acid and hydrogen sulphide do not appear to react, the solution remaining colourless, and regarded this phenomenon as due to the formation of an unstable compound, probably of molecular character, between the arsenious acid and the hydrogen sulphide. All the physical theories dealing with the colour of colloidal solutions regard change of this colour as dependent on one main factor, namely, the dimensions of the colloidal particles. Zsigmondy's experiments on colloidal gold solutions ("Kolloidchemie," 1912) showed, however, that in many cases marked changes in the colour cannot be explained by alteration of the

magnitude of the particles, especially as Mie's experiments (*Ann. Physik*, 1908, [iv], **25**, 377—445) indicate that the size of the colloidal gold particles may vary within comparatively wide limits without being accompanied by marked displacement of the maximum of the absorption spectrum. Zsigmondy assumed it to be possible, therefore, that the colour of a colloidal solution may be influenced also by the distribution of the particles throughout the dispersive medium.

The author has carried out various series of experiments in this direction on colloidal arsenious sulphide solutions, more particularly Vorländer's colourless modification. The results show that change of colour with these solutions depends in far higher degree on the distribution of the colloidal particles in the medium than on the magnitude of the particles. Further, observations on the stability of the separate solutions explain the two directions in which this change of distribution may take place; these the author terms "aggregation" and "disaggregation" of the particles. In the former case, that is, when the particles combine to form separate complexes or aggregates, the colour of the solution darkens, and, at the same time, its stability diminishes, such union of the particles being the first step towards coagulation. In the latter case, that is, when the particles strive more and more towards individual existence, until in the limit each of them occurs in the disperse medium completely separated from the others, the solution becomes paler and more stable. The preparation of quite colourless solutions of arsenious sulphide requires the presence of a stabilising substance, which in this particular instance is an excess of the arsenious acid. This colourless solution contains, not, as Vorländer and Haberle supposed, a molecular compound, but ordinary arsenious sulphide in the colloidal state. The lack of colour is conditioned by the simultaneous action of two factors, the extremely small magnitude of the particles and, more especially, the complete individuality of these particles. T. H. P.

The Influence of the Quantity of Peptonising Agent on the Properties of Hydrosols. Hydrosol of Stannic Acid. R. Zsigmondy (*Zeitsch. anorg. Chem.*, 1914, **89**, 210—223).—Stannic acid hydrosol, 0·5% SnO_2, prepared by the dialysis of stannic chloride, is peptonised by varying quantities of potassium hydroxide, free from carbonate. The ratio $K_2O : SnO_2$ is varied from 1 : 2 to 1 : 200. The various properties vary in the same order. With increasing proportions of the peptonising agent, the size of particles, electrically transported stannic acid, gold number, and viscosity decrease. The stability on boiling, osmotic pressure, conductivity, and quantity of electrolyte required for precipitation increase. The surface tension remains constant or decreases slightly.

The greatest opalescence is shown by the solutions containing least alkali, and these are retained by the ultra-filter, whilst the most alkaline solutions past through completely. The residue on

the ultra-filter contains the alkali, and redissolves readily in water, but undergoes irreversible changes on drying.

The results are in accordance with the author's theory of peptonisation. C. H. D.

Determination of the Size of Ultramicroscopic Particles in Suspension in a Liquid, by a Chronophotographic Method. G. Rebière (*Bull. Soc. chim.*, 1915, [iv], **17**, 155—163).—The author has devised an apparatus to replace the ordinary cinematograph apparatus to photograph the movement of ultramicroscopic particles.

In applying the ordinary formula for Brownian movement, $\Delta^2x=RT/N\,.\,t/3\pi\eta r$, to the determination of the radius of ultramicroscopic particles, if the general constants are replaced by their value, and the medium used is water at 20°, having a viscosity $\eta=0{\cdot}01$, then r can be evaluated from the resulting equation, $r=37\times10^{-14}t/\Delta^2x$, providing t and Δx can be measured.

The cinematograph apparatus described by Henri (compare A., 1908, ii, 760) has certain disadvantages in that (1) the time between the taking of two successive images cannot be accurately measured; (2) the films are unsuitable for photographing coloured objects of the type of some colloidal particles; (3) these films, if used, alter their dimensions during the processes of development, fixing, washing, and drying, thus vitiating subsequent measurements.

The apparatus described remedies these defects in that it permits of the use of a panchromatic plate, on which ten images can be projected by an ultramicroscope and taken at intervals of time exactly known. In essential details it consists of a plate carrier drawn by an electromagnetic, and a shutter controlled by an electromagnet, the two systems being controlled by a metronome, with an electrical contact, in such a way that when the carrier is at rest the shutter is open and the photograph taken, and, the shutter being closed, the carrier is moved vertically upwards a distance equal to the height of the image. Cross-wires in the aperture cast their shadow on the plate and serve as reference lines for subsequent measurements, after the negative has been enlarged, by means of a measuring machine. Allowing for the enlargements due to the ultramicroscope and the camera, the value of Δx can be determined for a number of grains, and t being measured by the metronome, r can be calculated.

The author has used this instrument to measure the size of the largest and smallest grains in a solution of colloidal sulphur, the values obtained being, for the large particles, $r=144{\cdot}9\times10^{-7}$, and for the small particles $r=13{\cdot}4\times10^{-7}$. W. G.

Action of Neutral Salts on the Constant of Chemical Equilibrium. G. Poma and G. Albonico (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 747—754. Compare A., 1911, ii, 707; 1914, ii, 440; this vol., ii, 210).—The authors have determined the influence of lithium chloride on the reaction

$$CH_3{\cdot}CO_2H+Me{\cdot}OH\rightleftarrows H_2O+CH_3{\cdot}CO_2Me$$

in aqueous methyl-alcoholic solutions, 0·2*N*-hydrochloric acid being used as catalyst. In the equilibrium position,

$$K = k_2/k_1 = (a-x)(b-x)/(c+x)(d+x),$$

where a, b, c, and d are the initial molar concentrations of the reacting compounds, and x the diminution in concentration of the alcohol or acid. No methyl acetate being taken initially, the condition at an intermediate stage of the hydrolysis is expressed by $dx/dt = k_1(a-x)(b-x) - k_2x(c+x)$. Replacing

$$(a+b+cK)/(1-K)$$

by α, and $ab/(1-K)$ by β, this gives $(k_1-k_2)dt = dx/(x^2-\alpha x+\beta)$. Integration of this expression yields

$$k_1-k_2 = 1/(\zeta-\xi)t \,.\, ln\, \xi(x-\zeta)/\zeta(x-\xi),$$

where ζ and ξ are the roots of the equation $x^2-\alpha x+\beta=0$. This equation, and that for k_2/k_1, give the separate values of k_1 and k_2.

It is found that the presence of lithium chloride, even in an aqueous alcoholic solvent, exercises an accelerating influence on the velocities of both esterification and hydrolysis. Such action is, however, of different magnitudes for the two reactions; thus, the presence of 3 mols. of lithium chloride per litre increases k_1, the velocity constant of esterification, from 0·00240 to 0·00594, whilst k_2 increases from 0·00041 only to 0·00064. Consequently, the equilibrium constant, K, diminishes from 0·170 to 0·108. Thus, the influence of the lithium chloride is not that characteristic of catalytic action, but has an effect such as would be produced if the salt removed part of the water present in the system from the immediate play of the equilibrium. T. H. P.

Equilibria in Ternary Systems. XVIII. F. A. H. Schreinemakers (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1260—1274. Compare this vol., ii, 46).—A further discussion of the equilibrium relations characteristic of certain ternary systems. H. M. D.

Equilibria in the Systems α-Naphthylamine-Guaiacol and Urethane-Benzene. N. A. Puschin and G. N. Mazarovitsch (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1366—1372).—The diagram of state of the system α-naphthylamine-guaiacol is characterised by the formation of: (1) a compound, $OH\cdot C_6H_4\cdot OMe, C_{10}H_7\cdot NH_2$, m. p. 21·4°, and (2), two eutectics, one, m. p. 19·8°, containing 40 mol. % of guaiacol, and the other, m. p. 14·3°, 77 mol. %. Solid solutions are probably formed only in the interval from 43 to 50 mol. % of guaiacol.

The system urethane-benzene forms a eutectic containing 97 mol. % at 4·2°, and solid solutions in the interval from 97 to 100 mol. % of benzene. T. H. P.

Inflammable Limits of Mixtures of Gasolene Vapour and Air. George A. Burrell and Hugh T. Boyd (*J. Ind. Eng. Chem.*, 1915, **7**, 414—417).—The lower limit of complete inflammation lay between 1·9 and 2% of gasolene vapour (from gasolene of 73° B.) when the mixture was ignited from the top; the upper limit was

between 5·2 and 5·3% of gasolene vapour. When ignited from the bottom by means of an electric spark, the lower limit was 1·4 to 1·5% of gasolene vapour, and the higher limit 6·0 to 6·4%. Practically the same limits were obtained on using the vapour from "cleaners' naphtha" (59—60° B.). When the initial temperature was increased before igniting the mixtures, the lower limit was decreased until, at 400°, it lay between 1·02 and 1·22% of gasolene vapour. W. P. S.

Influence of Temperature and Pressure on the Explosibility of Methane–Air Mixtures. G. A. Burrell and I. W. Robertson (*J. Ind. Eng. Chem.*, 1915, **7**, 417—419).—When the initial temperature of methane-air mixtures is 500°, the lowest limit for the complete propagation of flame is between 3·75 and 4·00% of methane; the limit decreases as the temperature falls, until at ordinary temperatures it is about 5% methane. Increased pressure up to 5 atmos. has no effect on the lowest limit of complete propagation of flame in the mixture. W. P. S.

Halogen Oxygen Compounds. X. Kinetics of Bromate Formation from Bromine. Anton Skrabal and Siegfried R. Weberitsch (*Monatsh.*, 1915, **36**, 237—256. Compare this vol., ii, 330).—The rate of reaction of the formation of bromate from bromine in the presence of alkali and bromine ions has been determined at 25°. As alkali, a mixture of Na_2HPO_4 and NaH_2PO_4 or $KHCO_3$ and Na_2CO_3 was used; measurements were also made in the presence of sodium nitrate. The reaction is shown to occur according to two schemes: (1) $3Br_3' + 6OH' = 8Br' + BrO_3' + 3H_2O$, and (2) $3Br_2 + 6OH' = 5Br' + BrO_3' + 3H_2O$. It is shown that the velocity of formation of bromate increases with increase of the hydroxyl ion and bromine concentration, but decreases with increase in the bromidion concentration. The rapid reaction follows the time relationships

$$-d(Br_3')/dT = k_1[OH']/[Br_3']\cdot[Br_3']^2$$

and $-d[Br_2]/dT = k_1'[OH']/[Br']\cdot[Br_2]^2$, whilst the slow reaction follows the relationships $-d[Br_3']/dT = k_2[OH']^4/[Br']^7\cdot[Br_3']^3$ and $-d[Br_2]/dT = k_2'[OH']^4/[Br']^4\cdot[Br_2]^3$. The temperature-coefficient of the slow reaction in the phosphate mixture is about 17. J. F. S.

Aspirin. II. The Formation of Aspirin. D. E. Tsakalotos and S. Horsch (*Bull. Soc. chim.*, 1915, [iv], **17**, 186—190. Compare this vol., ii, 47).—The authors have measured the velocity of action of acetic anhydride on salicylic acid in benzene solution at three different temperatures, namely, 25°, 30°, and 50°, by determining the acidity produced by running aliquot portions of the mixtures into water at definite intervals of time. $N/50$-Barium hydroxide was used as the standard alkali, and phenolphthalein as indicator. The results show that the reaction is one of the second order, the coefficient of temperature for 10° being 2·2. The acceleration of the velocity of formation of aspirin has

a limit, since above 90° the aspirin formed begins to decompose, giving acetic anhydride and salicylsalicylic acid. W. G.

Velocity of Self-Esterification of Dibasic Acids. ANTON KAILAN (*Zeitsch. physikal. Chem.*, 1915, **89**, 641—684).—The molecular conductivity of oxalic acid, malonic acid, tartaric acid, maleic acid, and fumaric acid has been determined at 25° in absolute alcohol and in alcohol containing 0·022, 0·69, and 1·40 mols. of water per litre. The measurements were carried out for several concentrations in each case, and from the results the dissociation constant has been calculated. The strength of the acids is thus shown to be in the order maleic, oxalic, malonic, tartaric, fumaric, whilst for aqueous solutions the order is oxalic, maleic, malonic, fumaric, and tartaric. The rate of self-esterification in absolute alcohol and in aqueous alcohol has been determined at 25° for the above-mentioned acids and for malic acid. It is found that at the commencement of the reactions the velocity is not proportional to the square of the concentration, but to the power of 3/2 of the concentration, and consequently the reaction is not bimolecular, but sesquimolecular. A calculation is made to estimate the fraction of the reaction which is due to the hydrogen ions, from which it is shown that a considerable proportion of the reaction is due to the hydrogen ions, which, in the case of maleic and oxalic acids, does not exceed 50—70% of the total reaction. The sesquimolecular reaction does not increase with increasing concentration of the acid, and this is explained by the assumption that in the self-esterification of dibasic acids, in addition to two reactions which occur in the self-esterification of monobasic acids, a third comes into force here, namely, that the one carboxyl group of the acid esterifies the other carboxyl group of its own molecule, just as it esterifies the carboxyl group of another molecule. The statement of Snethlage (A., 1913, ii, 1044), that the relative catalytic action of the undissociated acid increases with increasing strength of the acid, is found to hold for dibasic acids, and appears also to be true for the third reaction. The retarding action of small quantities of water is different in the different cases, but is always small, and sometimes hardly noticeable. The order of the velocity of self-esterification is not the same as that of the esterification in the presence of hydrogen chloride (A., 1914, ii, 41). If, however, the product of the reaction constant in the presence of hydrogen chloride and the equivalent conductivity of the acid is obtained, then a series of the acids is obtained which is the same as that of the velocities of self-esterification of the acids. This points to the fact that steric influences play a considerable part, particularly in the indirect esterification. J. F. S.

Indirect Ester Formation in Aqueous Alcohol. ANTON KAILAN (*Zeitsch. physikal. Chem.*, 1915, **89**, 676—684.)—A series of measurements of the equivalent conductivity of hydrochloric acid in absolute alcohol, and in alcohol containing 12·3%, 25%, 50%, and 75% by volume of water, have been made at 25°. The velocity

of esterification of succinic acid has been determined in alcohol of the above-named concentrations and in the presence of hydrochloric acid. In the calculation, account is taken of the hydrolysis of the ester formed. It is shown that k_1, the esterification constant, is not proportional to the concentration of hydrochloric acid when small concentrations of water are present, but at 28% is almost strictly proportional. With increasing water content, the velocity of esterification decreases, and is approximately inversely proportional to the water concentration. The hydrolysis constant, k_2, decreases approximately inversely proportional to the water concentration down to water = 28 mols., but from this value downwards it is approximately constant. In the presence of 1/6*N*-hydrochloric acid, succinic acid is esterified by an alcohol–water mixture which contains 25 or 50 vol. % of water 100 or 150 times more slowly than in an alcohol–benzene mixture containing the same amount of alcohol (A., 1914, ii, 641). J. F. S.

Velocity of Hydrogenation of Tetramethylbutinenediol in Presence of Colloidal Palladium and in Various Solvents. J. S. Zalkind and P. V. Pischtschikov (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1527—1539).—It has been previously shown (A., 1914, ii, 257) that, in presence of colloidal palladium, acetylenic glycols combine first with two atoms of hydrogen, yielding glycols of the ethylene series; further combination with hydrogen, if it takes place, proceeds comparatively slowly. The influence of the conditions of the reaction on the velocity of hydrogenation of the treble linking has now been investigated in the case of tetramethylbutinenediol.

It was shown by Fokin (A., 1908, i, 311) that, in presence of platinum-black, combination with hydrogen at a double linking follows the law for monomolecular reactions, and the same holds also for hydrogenation of acetylenic glycols in presence of platinum (compare Zalkind, *loc. cit.*). With the previous experiments, in which 5 grams of the glycol, 0·01 gram of palladium, and 50 c.c. of alcohol were taken, this rule was approximately obeyed. It is now found, however, that when a few milligrams of colloidal palladium are taken per 0·01 gram-mol. of the glycol, the value of k, calculated from the equation for monomolecular reactions, undergoes marked increase. In the case of certain enzymic reactions, Henri (A., 1902, ii, 127) showed that the law followed is expressed by the equation $k_1(1+\epsilon x) = 1/t \cdot \log[(a+\epsilon x)/(a-x)]$, where t is the time, a the initial amount of the substance acted on, k_1 the constant of the reaction, and ϵ a constant characterising the catalytic effect of some new factor. If ϵ is made equal to 2, the authors' results gives values for k_1 which are virtually constant, especially up to the time when 90% of the initial compound has reacted.

Experiments were made at 3°, 10°, 17·5°, 20°, 25°, and 30°, the other conditions being precisely similar in all cases. The dependency of k_1 on the temperature is found to be rectilinear within the limits of accuracy of the measurements. The tempera-

ture-coefficient, $k_1^{20}/k_1^{10}=1\cdot75$, a value approximating to that usual in chemical reactions; the chief part in the process considered is, therefore, a chemical influence. With varying and small proportions (up to 0·001 gram) of the colloidal palladium, the velocities of the reaction increased with, but more rapidly than, the amounts of the catalyst; for instance, when the latter were in the ratios 1 : 1·25 : 1·67, the corresponding velocities were in the ratios 1 : 1·67 : 2·67. With 0·002—0·010 gram of palladium, the velocities are approximately proportional to the amounts of the catalyst present. Similar rapid increases in the velocity of reaction as the amount of the catalyst is increased were observed with the decomposition of hydrogen peroxide in presence of colloidal platinum (compare Bredig and Müller von Berneck, A., 1900, ii, 213) or colloidal gold (compare Bredig and Reinders, A., 1901, ii, 442), only small amounts of catalyst being employed.

When fixed amounts of the glycol and palladium are taken, there is a certain concentration at which the velocity is a maximum, use of a greater or less quantity of solvent resulting in retardation of the reaction. That the solvent itself exerts a catalytic influence is shown by the following values of k_1 obtained with different solvents: water, 0·033; ethyl alcohol, 0·044; methyl alcohol, 0·060.

The increase which occurs as the reaction proceeds in the value of k, calculated from the formula for monomolecular reactions, is shown to be due, not to the presence of the ethylenic glycol formed, but to the gradual removal of the acetylenic glycol, which acts as a negative catalyst. T. H. P.

Rate of Hydration of Camphoric Anhydride. Bernard Howell Wilsdon and Nevil Vincent Sidgwick (T., 1915, **107**, 679—682).—Measurements have been made of the electrical conductivity of aqueous solutions of camphoric acid, and these data employed in the determination of the rate of hydration of camphoric anhydride at 18° and 25°. The ionisation constant of the acid is 0·00236 at 18° and 0·00198 at 25°. The hydration of the anhydride takes place in agreement with the equation for a monomolecular reaction, for which k at 18° = 0·0000975 and k at 25° = 0·000158.

When the solution is in contact with excess of the anhydride, the rate of formation of the acid is constant. By observations under these conditions, the influence of alkali on the rate of hydration was examined. The results obtained show that the velocity of hydration at 25° in presence of $N/200$-alkali is approximately 10,000 times as great as the velocity in pure water. H. M. D.

The Velocity of Reduction of Potassium Permanganate by Oxalic Acid. A. Boutaric (*Compt. rend.*, 1915, **160**, 711—714. Compare Harcourt and Esson, *Phil. Trans.*, 1866, **156**, 193).—A determination of the velocity of reduction of aqueous potassium permanganate by oxalic acid in the presence

of sulphuric acid by means of spectrophotometric measurements of the intensity of the transmitted light of a given wave-length ($\lambda = 558\,\mu\mu$) in the region where the absorption due to the permanganate begins to be felt. The results show that the velocity of the reaction at any instant is not proportional to the quantity of unchanged permanganate at that instant, but that it starts from zero, increases to a maximum, and then decreases to zero. The results are the same for very different proportions of reagents used. The presence of an excess of sulphuric acid or oxalic acid simply accelerates the reaction. W. G.

Kinetics of Chemical Reactions. X. E. I. Orlov (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1441—1481).—The author applies the considerations previously developed (A., 1912, ii, 243; 1913, ii, 127, 128, 681, 682, 683, 938; 1914, ii, 638) to the results obtained by Millar (A., 1913, ii, 1041), Braune (A., 1913, ii, 1042), and Snethlage (A., 1913, ii, 1044), the velocity constants of the decomposition of methyl and ethyl diazoacetates being calculated from the formula $0{\cdot}4343mk = 1/t \,.\, \log[A/(A - mx)]$. The results of the calculations show that the catalytic decomposition of diazoacetic esters in alcoholic and aqueous-alcoholic media under the influence of picric acid as catalyst proceeds according to the law $dx/dt = k(A - mx)$. As regards the reaction in anhydrous alcoholic solutions, it may be assumed that the action of the picric acid is directly proportional to its concentration and its ionisation, so that $c_1\alpha_1/c_2\alpha_2 = k'/k''$. Examination of the experimental data on these lines shows that the velocity constants of a chemical reaction, proceeding under the influence of a catalyst in alcoholic and aqueous-alcoholic solutions, together with a knowledge of the electrolytic dissociation of the catalyst in these solutions, render it possible to calculate the percentage distribution of the hydrogen ions of the catalyst between the alcohol and the water, to deduce the law according to which the distribution varies as the proportion of water is increased, and thus to find the distribution constants. It is found that the distribution of the hydrogen ions of the catalyst between the alcohol and the water obeys the same law of mass action as that playing a dominant part in kinetic phenomena. This result serves to confirm the validity of the solvate theory. In the catalytic decomposition of diazoacetic esters, the hydrogen ions of only one catalyst take part, so that the kinetic data furnish a trustworthy means to calculate the distribution of the hydrogen ions between water and alcohol. In the formation of esters under the influence of a catalyst, the solution always contains, in addition to the hydrogen ions of the catalyst, ions of the organic acid, the distribution constants of the hydrogen ions depending in this case also on the nature of the organic acid. T. H. P.

The Velocity of Solution of Blende and Galena in Dilute Sulphuric Acid. Felix Rosenkränzer (*Zeitsch. anorg. Chem.*, 1914, **88**, 452).—The figures formerly given (A., 1914, ii, 640)

should have been calculated for equal volumes instead of for equal weights. The conclusions are not affected, but the ratios should be altered, that of galena to Spanish blende being 1 : 3·2 instead of 1 : 5·8. C. H. D.

Contact Action of Water Vapour and Carbon in the Oxidation of Ferrous Compounds. A. G. Doroschevski and A. Ja. Bardt (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1669—1676. Compare this vol., ii, 331).—The charcoal used in the industrial purification of alcoholic liquids is always stored in a dry place, exposure to moisture resulting in a loss of activity. The authors find, however, that such loss is not occasioned by access of moisture to the charcoal.

The oxidation of ferrous compounds in presence either of water vapour or carbon alone, or of both of these together, has been investigated. In absence of water vapour, carbon does not oxidise ferrous to ferric oxide at the ordinary temperature, so that the activity of charcoal as an oxidising agent should not diminish in dry air. When mixed with carbon and placed in a desiccator over water, ferrous oxide becomes completely oxidised only after some months at room temperature, but after some days at 39—41°. From the results of experiments on the oxidation of ferrous oxalate and sulphate in presence of water vapour and in presence or absence of charcoal, the authors draw the conclusion that the rôle of the carbon consists in intensifying the catalytic effect of the water vapour, and that the alcohol is involved in the reaction of conjugated oxidation. The carbon, in presence of water vapour, also undergoes oxidation at comparatively low temperatures.

T. H. P.

Activation of Chlorates by Formic Acid. K. A. Hofmann and K. Schumpelt (*Ber.*, 1915, **48**, 816—822).—In an earlier communication (Hofmann, A., 1913, ii, 62, 609) it has been shown that during the oxidation of carbon by solutions of chlorates in the presence of osmium tetroxide, the liquid becomes acidic, and appreciable quantities of chlorine peroxide are produced. At this stage of the process, the action increases in velocity, and it is now demonstrated that this effect is due to the formation of formic acid. If formic acid is added to a solution of a chlorate, the latter undergoes reduction to chlorine peroxide, which is produced more rapidly than it is removed, and so becomes free for other oxidation processes. In this way, substances which are not affected by a chlorate solution may be oxidised by a mixture of the chlorate with formic acid. The effect of the formic acid is due, not so much to its acidic character as to its reducing capacity, because acetic, tri-, and mono-chloroacetic and phosphoric acids do not possess this power.

The velocity of the reaction between potassium chlorate and an excess of formic acid was investigated by periodically withdrawing a small quantity of the mixture and estimating the iodine which this liberated from an acidified solution of potassium iodide.

Curves are given representing the results. It was observed that the reduction of the chlorine peroxide produced in the reaction occurs more rapidly under the influence of sunlight.

As examples of substances which may be oxidised by the mixture of chlorate and formic acid are mentioned indigotin (used as the sulphonic acid), aniline, and anthracene. D. F. T.

The Series Spectrum of Hydrogen and the Constitution of the Atom. L. VEGARD (*Phil. Mag.*, 1915, [vi], **29**, 651—655).—According to Allen (this vol., ii, 33), the deviations of the series lines of hydrogen from the Balmer formula can be explained if it is assumed that the core of the atom can produce a magnetic field equivalent to that set up by five or six magnetons. With certain modifications in the assumptions made by Allen, it is shown that the deviations may be accounted for by the magnetic influence of the inner core if a constant difference of momentum equal to p/π is supposed to be maintained between the outer and inner systems of electrons. The assumption of a core of five magnetons would involve the storing of a quantity of energy enormously greater than the energy of the outer electron, and it seems scarcely possible to admit that a system with so much energy would be appreciably affected by the passage of the outer electron from one stationary state to another. H. M. D.

An Atomic Model with a Magnetic Core. H. STANLEY ALLEN (*Phil. Mag.*, 1915, [vi], 714—724. Compare this vol., ii, 33).—The view that it is necessary to take account of magnetic as well as electrostatic forces in devising an atomic model has been further elaborated, and an atomic model is suggested which consists of a ring or rings of electrons surrounding a central core which has a radius much greater than that of the Rutherford atom, and is, in consequence, capable of producing appreciable magnetic forces in its vicinity. The total charge of the core is equal to Ne, where N is the atomic number. The magnetic moment of the core arises from the orbital motion of the discrete electrified particles of which it is composed. The fact that α- and β-particles are derived from the nucleus of radioactive substances suggests that these exist in the nucleus as discrete particles, and in the author's model it is supposed that the revolving electrified particles consist of α-particles, β-particles, and hydrogen nuclei or positive electrons.

The diamagnetic properties of the atom are mainly determined by the external electrons revolving in orbits of radius equal to 10^{-8} cm. The so-called magneton is not an independent entity.

An attempt is made to ascertain the modifications which are required in Bohr's theory in order to obtain formulæ for spectral series applicable to elements other than hydrogen. It is suggested that the angular moment of certain parts of the core is associated with that of the external electrons concerned in radiation.

H. M. D.

Theory of Chemical Reaction and Reactivity. E. C. C. Baly (*J. Amer. Chem. Soc.*, 1915, **37**, 979—993).—A theory is proposed in accordance with which chemical reactivity and the chemical properties of atoms and molecules depend on the existence of molecular force fields due to the electromagnetic fields of the constituent atoms. All the phenomena of chemical reaction are regarded as attributable to the closed force fields and their opening up by the influence of solvents or light. The formation of differently coloured derivatives from the same compound is explained by the existence of definite stages in the opening up of a given complex field, each with its power of absorbing definite light rays. The theory indicates the existence of intermediate stages in a chemical reaction, and experimental evidence of such stages is adduced. When a compound is dissolved in a solvent, an equilibrium is established between the opened-up and non-opened-up molecules of the solute; such a system has the power of selectively absorbing light rays, the effect of the light being to increase the number of opened-up molecules, and thus to shift the equilibrium towards the reactive side. In support of this view, reference is made to certain experiments on the photocatalysis of the reaction between mercuric cyanide and potassium iodide. It is shown that the theory affords an explanation of allotropy, magnetic rotation, stereoisomerism, optical rotatory power, and the phenomena of isomerism generally. E. G.

The Systematic Doctrine of Affinity. VIII. The Dependence of Valency on Temperature. II. Wilhelm Biltz (*Zeitsch. anorg. Chem.*, 1914, **89**, 141—163. Compare A., 1909, ii, 875; this vol., ii, 465).—The rule that the valency isobars ascend the more steeply the lower the temperature is confirmed by an examination of the dissociation of the alkali oxides and of the hydrates of several salts. The rule that the tangents of the angles of inclination increase with falling temperature, but are constant at any one temperature for compounds of similar type, is confirmed by the hydrates of a number of salts. The chlorides give higher inclinations than the sulphates.

The ammonia compounds of thorium chloride fall into three groups, which obey the first rule separately, but not if the groups be regarded as one. The ammonia compounds of aluminium, samarium, and neodymium chlorides depart from the rule. In such cases, the higher and lower ammines are considered to be of different types. This also applies to the chlorides of platinum and iridium, platinum tetra- and tri-chloride, and iridium chloride belonging to one group, and platinum di- and mono-chloride and iridium tri-, di-, and mono-chloride to a different one. The higher chlorides are co-ordinated compounds. This is confirmed by the different behaviour of the two groups towards solvents. Reasons are given for doubting the high valencies assigned to sulphur, tungsten, and other elements. C. H. D.

The Nature of Subsidiary Valencies. IX. Influence of the Position of the Neutral Part of the Molecule on its Stability. FRITZ EPHRAIM (*Ber.*, 1915, **48**, 624—629. Compare this vol., ii, 166; A., 1914, i, 17, etc.).—A theoretical paper in which numerous examples are discussed to show that those factors which increase the stability of molecules with complex cations, notably the smallness of the central atom, work in exactly the opposite direction when molecules with complex anions are considered. For example, whilst salts of the complex metallohexammine cations decrease in stability with increasing atomic volume of the metal, the hydroxides, carbonates, nitrates, sulphates, and peroxides of the alkaline earths, which are regarded as containing complex anions, thus, $M[O(H_2O)]$, $M[O(CO_2)]$, $M[O(N_2O_5)]$, $M[O(SO_3)]$, and $M[O(O)]$, increase in stability with the atomic volume of the metal, as also do the polyhaloids or sulphides of the alkali metals.

The effect of the atomic volume of the central element in the cation is, therefore, very definite, but it is not yet certain what is exactly the effect of the atomic volume of the central atom in the anion, although the experiments in the seventh paper (A., 1914, i, 827) and in the following paper, on the acid haloids of organic bases, R[Hal.(HHal.)], suggest that it is about the same. Strictly speaking, a series like R[I(HF)], R[I(HCl)], R[I(HBr)], and R[I(HI)] should be examined, but such compounds cannot be obtained.

In non-ionisable complexes, similar rules hold good. Thus, $HgCl_2,2NH_3$ is more stable than $HgI_2,2NH_3$, and the stability of the additive compounds of stannic haloids with esters, ether, and acetonitrile decreases from the chloride to the iodide (Pfeiffer and Halperin, A., 1914, i, 923). J. C. W.

Some New Forms of Apparatus. I. Substitute for the Twin-bulb Trap in Toluene-Mercury Thermoregulators. P. B. DAVIS (*J. Amer. Chem. Soc.*, 1915, **37**, 1198—1199).—A form of apparatus is described which is intended to replace the ordinary twin-bulb device commonly employed in toluene-mercury thermoregulators. It is comparatively simple to construct, and has the advantages of being compact and not easily broken. Moreover, it is so arranged as to obviate all danger of the toluene creeping round between the mercury and the glass walls into the capillary and fouling the contact surface of the mercury. E. G.

Some New Forms of Apparatus. II. New Form of Pyknometer for Liquids. P. B. DAVIS and L. S. PRATT (*J. Amer. Chem. Soc.*, 1915, **37**, 1199—1200).—A new form of pyknometer has been devised which is free from the disadvantages of the ordinary Sprengel form. The reservoir is made of thin-walled glass tubing, and contains a thin glass tapering tube extending nearly to the bottom, and attached above to the outlet

tube of capillary bore. This tube facilitates drying and filling the instrument. The outlet tube is drawn out slightly at the end and bent at an angle of 60° at a point a little above the reservoir, and is slightly enlarged just below the bend in order to hold in position the wire used to suspend the pyknometer on the balance. The inlet tube, also of capillary bore, is sealed into the shoulder of the reservoir, and in its vertical portion has an expansion bulb of sufficient size to accommodate the increased volume of any liquid when the temperature is raised 10°; a fine line is etched round the capillary just below the bulb. The upper part of this tube is bent horizontally.

The pyknometer is more easily cleaned and dried than the old form. The projecting arms are short, and not easily broken, and the capillary tubes have been reduced to a minimum, thus decreasing the weight of the instrument. E. G.

Inorganic Chemistry.

The Spontaneous Crystallisation of Ice from Aqueous Solutions. RUDOLF HARTMANN (*Zeitsch. anorg. Chem.*, 1914, **88**, 128—132).—The crystallites of ice which separate from undercooled aqueous solutions are of three different types: hexagonal crystal skeletons, spherulites, and feathery growths. The first are formed when the degree of undercooling is small, the second when it exceeds a certain limit, whilst the third is the only form obtained when the solutions are very dilute, whatever be the degree of undercooling. The identity of the three forms is shown by the fact that undercooled pure water freezes at the same temperature when inoculated with any one of the three.

The hexagonal crystal skeletons are of two types, hexagonal plates with six rays, and rectangular plates with four rays, but in both cases the angles of intersection are only 60° and 120°, and the freezing point and linear velocity of crystallisation are identical. C. H. D.

Contribution to the Deacon Process. BERNHARD NEUMANN (*Zeitsch. angew. Chem.*, 1915, **28**, 233—236).—The double salt obtained by crystallising copper chloride with sodium chloride acts as a catalyst in the Deacon process at 300—500° in the same manner as copper chloride, and has the advantage of being less volatile and less readily fusible. Copper chloride commences to volatilise at 430—460°, and melts at about 500°, whilst the double salt first commences to sublime 80—90° higher. The temperature optimum for the production of chlorine, using the double salt as catalyst, is 470°, when the reaction velocity is so great that, using

a sufficient quantity of contact substance, equilibrium is attained during the passage of the gases. The equilibrium mixture at this temperature is richer in chlorine than when copper chloride is employed as catalyst, as the maximum possible temperature in that case is only 430°. Using a mixture containing 9·5% of hydrogen chloride, 84% was converted into chlorine, but this percentage naturally falls when gases containing a higher percentage of hydrogen chloride are employed. Although some improvement is attained by the use of the double salt, the author is of opinion that the process cannot be successful until a catalyst is found which functions efficiently at a much lower temperature.

G. F. M.

The Richness of the Atmosphere in Oxygen According to Guye and Germann. A. LEDUC (*Compt. rend.*, 1915, **160**, 710—711. Compare A., 1891, 1416).—Recalling his results obtained twenty-four years ago by the same method, the author considers that the value obtained by Guye and Germann for the oxygen content of the atmosphere at Geneva (compare A., 1914, ii, 740) is probably too low. W. G.

The Relation of the Oxygen Tension of the Atmosphere to Combustion. H. C. DALLWIG, A. C. KOLLS, and A. S. LOEVENHART (*Proc. Amer. Soc. Biol. Chem.*, 1914; *J. Biol. Chem.*, 1915, **20**, xxxii—xxxiii).—Nitrogen inhibits combustion, apart from its action as a diluent. Thus, a candle is extinguished at an oxygen pressure of 116·4 mm. when nitrogen is added, whereas it does not go out until 19·8 mm. if the lowering is effected by evacuation. In vital processes, the oxidation depends purely on oxygen tension. W. D. H.

Investigations on Ammonia. VII. The Action of Uranium as Catalyst in the Synthesis of Ammonia from its Elements. F. HABER and H. C. GREENWOOD (*Zeitsch. Elektrochem.*, 1915, **21**, 241—245. Compare this vol., ii, 411).—Haber and Le Rossignol (A., 1908, ii, 362) have shown that ammonia is produced when a mixture of nitrogen and hydrogen passes over uranium which contains carbon, and at the same time the uranium takes up nitrogen and falls to powder. The present paper deals with the action of uranium in the formation of ammonia. It is shown that when a mixture of nitrogen and hydrogen is passed over uranium carbide at about 500° and under high pressure uranium nitride is formed, the major portion of which dissolves in acids with the formation of ammonia, whilst a small portion is insoluble, and is only decomposed by boiling with concentrated alkali. As the nitride formation proceeds, the contact material falls to a fine powder, and after prolonged use forms a hard, compact mass, the catalytic action increasing. A study of the volume-time efficiency of the uranium catalyst has been made, and it is shown that this increases very much with increase of pressure. A small scale apparatus is described, based on apparatus previously

employed for the preparation of pure ammonia from nitrogen and hydrogen. J. F. S.

Behaviour of Certain Hydrazine Salts on Decomposition by Heat. J. W. TURRENTINE (*J. Amer. Chem. Soc.*, 1915, **37**, 1105—1114).—Sabanéeff (A., 1899, ii, 365) has shown that azoimide is produced by the decomposition of hydrazine nitrate and dinitrate. The decomposition of some other hydrazine salts has now been studied.

When a neutral solution of hydrazine chlorate is heated, azoimide is not produced, but it is readily obtained on heating a solution acidified with sulphuric acid. The dichlorate yields azoimide both in presence and absence of sulphuric acid, but the mono- and di-perchlorates do not give azoimide in either case. When the dry, crystalline diperchlorate is decomposed by heat in a current of carbon dioxide, azoimide is produced, but the monoperchlorate does not yield any azoimide under these conditions; in each case, chlorine, nitrogen, oxygen, hydrogen chloride, and water are produced. The normal and acid sulphates are decomposed under these conditions with formation of water, hydrogen sulphide, sulphur dioxide, and sulphur, but azoimide is not obtained.

Azoimide can be detected in presence of sulphites by the following method, which depends on the fact that azoimide is not oxidised by hydrogen peroxide in presence of alkali hydroxide. The solution is treated with sodium hydroxide and hydrogen peroxide, boiled until effervescence ceases, and then acidified with sulphuric acid and distilled. The distillate is tested for azoimide by means of ferric chloride. E. G.

Electrochemical Oxidation of Hydrazine Sulphate and Ammonium Hydroxide. J. W. TURRENTINE and J. M. OLIN (*J. Amer. Chem. Soc.*, 1915, **37**, 1114—1122).—Szarvasy (T., 1900, **77**, 603) has found that hydrazine is decomposed on electrolysis with liberation of nitrogen and hydrogen in the ratio $N_2 : 2H_2$. Experiments have now been made under varying conditions to ascertain whether reactions could be induced by electrolysis which would yield azoimide.

The results have shown that when a saturated solution of hydrazine sulphate containing 10% by volume of concentrated sulphuric acid is submitted to electrolysis, azoimide and ammonia are produced if a high current density is maintained at the anode. The yield of azoimide is increased if the solution is kept at 0° during electrolysis. Since these conditions favour the formation of persulphates, it is considered that the oxidation is the result of a secondary anode reaction in which the persulphate ion, produced in a primary anode reaction, reacts with the hydrazine ion. The quantity of azoimide produced in some of the experiments was estimated.

Ammonium hydroxide, in presence of sodium chloride and glue and with low current density, is oxidised electrochemically to

hydrazine if the sodium chloride is added gradually in small quantities during the electrolysis. E. G.

Description of the New Compound, Hydrazine Diperchlorate. J. W. TURRENTINE [with A. C. GILL] (*J. Amer. Chem. Soc.*, 1915, **37**, 1122—1128).—Hydrazine chlorate and perchlorate have been described by Salvadori (A., 1907, ii, 759). An account is now given of the dichlorate and diperchlorate.

Hydrazine dichlorate, $N_2H_4,2HClO_3$, was obtained by treating a solution of hydrazine hydrogen sulphate, N_2H_4,H_2SO_4, with the calculated quantity of barium chlorate, filtering, and evaporating the solution in a vacuum at 0°. As soon as the crystals began to appear, however, decomposition took place, with evolution of chlorine.

Hydrazine diperchlorate, $N_2H_4,2HClO_4,2H_2O$, obtained by the interaction of barium perchlorate and hydrazine hydrogen sulphate, forms colourless, tabular, orthorhombic crystals, which effloresce in dry air but deliquesce in moist air. At 29°, 100 parts of water dissolve 102 parts of the hydrated salt. It is soluble in alcohol to the extent of 2·8 parts in 100, and in ether to the extent of 1 part in 100 parts of the solvent. The salt begins to melt at 95°, but undergoes decomposition before it is completely melted. Solutions of hydrazine diperchlorate are strongly acid, and decompose carbonates. The dichloride and dichlorate also show acid properties, and all these salts can be estimated by titration with solutions of alkali hydroxide in presence of methyl-orange, just as Stollé has shown to be the case with the hydrogen sulphate (A., 1903, ii, 101). E. G.

Hydrazine. [Sodium Hydrazide and a Case of Isomerism between Two Simple Derivatives of Hydrazine.] W. SCHLENK and TH. WEICHSELFELDER (*Ber.*, 1915, **48**, 669—676).—When thin slices of sodium are gradually added to ordinary free hydrazine in an atmosphere of pure, dry nitrogen, a colourless precipitate is formed, and the liquid develops a yellow colour. The deposit is sodium hydroxide, for the best hydrazine still contains some hydrate.

By treating hydrazine in this way until the yellow colour was permanent, and then distilling the hydrazine in a vacuum, the authors have obtained absolute hydrazine, which then dissolved sodium completely with the evolution of ammonia and a little hydrogen. On evaporating the yellow solution, *sodium hydrazide*, $NH_2{\cdot}NHNa$, remained as a residue of glistening leaflets. It was found to be most violently explosive. A mere breath of air, or a trace of moisture or alcohol, sufficed to produce disastrous results. The substance was analysed, however, by covering it with much dry benzene and very gradually adding benzene containing a little alcohol until the solid had given place to a solution of hydrazine and sodium ethoxide in alcohol, when water was added, and the ratio between the sodium and nitrogen was estimated. Complete details of a special apparatus are given.

When hydrazine is mixed with methyl alcohol, heat is developed,

and, on cooling with solid carbon dioxide, a mass of colourless needles is obtained. The mixture has no definite b. p., however, the affinity of hydrazine for alcohol being much smaller than the affinity for water. Hydrazine methyl alcoholate, $[NH_2 \cdot NH_3]OMe$, is isomeric with methylhydrazine hydrate, $[NH_2 \cdot NH_2Me]OH$.

J. C. W.

Boiling Point of Aqueous Solutions of Nitric Acid at Different Pressures. I. HENRY JERMAIN MAUDE CREIGHTON and JOHN HORACE GITHENS (*J. Franklin Inst.*, 1915, **179**, 161—169).—Determinations of the boiling points and vapour pressures of mixtures of nitric acid and water have been made at atmospheric and diminished pressures, using the dynamical method, the mixtures being heated in a flask similar to that described by Young (T., 1902, **81**, 772). For diminished pressures, the flask was connected through reflux condensers with a large bottle containing solid sodium hydroxide, which, in its turn, was in communication with a mercury manometer, and, through a series of wash flasks containing sodium hydroxide solution and sulphuric acid, with a vacuum pump. Tables are given showing the boiling points of 99·79% nitric acid ($D_4^{25} = 1{\cdot}5049$) at various pressures, and the boiling points of aqueous nitric acid of strengths from 19·37% upwards at 760, 360, 250, and 110 mm. pressure, from which the variation of the vapour pressures at various temperatures with the molecular percentage of nitric acid is calculated. Numerous curves are given, from which it is evident that the composition of the mixture of maximum boiling point varies but slightly with the pressure, namely, 68·18% nitric acid boiling at 121·7°/760 mm., 67·15% boiling at 99·9°/360 mm., and 66·8% boiling at 74·2°/110 mm. An examination of the curve showing the vapour pressures of mixtures at various temperatures shows that the square root of the product of the vapour pressures of water and pure nitric acid for any given temperature is always greater than the vapour pressure of any mixture of nitric acid and water at that temperature, as would be expected of liquids which form mixtures of maximum boiling point.

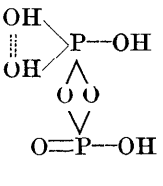
G. F. M.

The Structure of Pyrophosphoric Acid. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1914, **88**, 133—150).—The properties of pyrophosphoric acid indicate an unsymmetrical structure. Disodium hydrogen orthophosphate is converted into sodium pyrophosphate at 250±2°, and the temperature of the change is unaffected by the use of a dry atmosphere or of one saturated with water vapour at 95°; 250° is, therefore, the melting point of the orthophosphate.

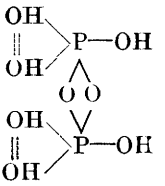
The ionisation constants of the first two hydrogen ions of pyrophosphoric acid are practically identical. Those of the third and fourth hydrogen ions are near to one another, but widely different from the first, which is near to that of the first ion of orthophosphoric acid.

The conditions of dehydration (A., 1910, ii, 607) indicate the

following probable formulæ for pyrophosphoric (I) and orthophosphoric acid (II):



(I.)



(II.)

The reactions of the compound $P_2O_3Cl_4$ also suggest an unsymmetrical structure: its decomposition into $POCl_3$ and PO_2Cl when distilled under 10 mm. pressure, and the fact that it reacts more violently with water than $POCl_3$, in spite of its formation from $POCl_3$ and water.

Ethyl pyrophosphate decomposes on distillation, yielding ethyl orthophosphate, metaphosphoric acid, and ethylene. The ester reacts with phosphorus pentachloride on heating, yielding a chloroester with ethylene, ethyl chloride, and PO_2Cl. $POCl_3$ is not formed. This behaviour is consistent with either formula.

Sodium pyrophosphate reacts with phosphorus pentachloride in a sealed tube above 200°, 3 mols. of pentachloride being decomposed, without the formation of P_2O_5:

$$Na_4P_2O_7 + 3PCl_5 = NaPO_3 + 3NaCl + 4POCl_3.$$

This reaction is only accounted for by the unsymmetrical formula.

Silver pyrophosphate becomes yellow at 130°, and is then partly converted into metaphosphate. The double salt, $NaAg_3P_2O_7$, decomposes on melting, giving Ag_3PO_4 and $NaPO_3$. C. H. D.

Action of Bromine on Carbon Monoxide. A. Piva (*Gazzetta*, 1915, **45**, i, 219—237).—In conjunction with Levi, the author (A., 1914, i, 480) found that the use of bromine water for the detection of unsaturated hydrocarbons in presence of large proportions of carbon monoxide yields uncertain results. In view of the contradictory statements which have been made concerning the formation of carbonyl bromide from carbon monoxide and bromine, the author has investigated the conditions under which these compounds interact. The extent to which the action proceeds under the influence of sunlight depends on the proportion of moisture present, and when special care is taken to dry the bromine and carbon monoxide, the velocity of the change is extremely low. Were complete absence of moisture attainable, it appears probable, but is not certain, that no reaction would occur. The reaction yields carbon dioxide and hydrogen bromide as final products, and takes place in two stages, $CO + Br_2 = COBr_2$ and $COBr_2 + H_2O = CO_2 + 2HBr$. In the first stage, equilibrium is reached with a small concentration of the carbonyl bromide, which must be removed as it is formed in order that the reaction may continue. T. H. P.

Microscopy of Metals with the Aid of Polarised Light. H. HANEMANN (*Zeitsch. anorg. Chem.*, 1914, **88**, 265—268. Compare A., 1913, ii, 1055).—For the examination of single micrographic constituents, the smaller form of apparatus is preferred. A quartz plate is used, and the Nicols are adjusted to give the sensitive violet tint. On rotating the object, anisotropic substances show a change of tint. Greater sensitiveness is obtained by using a Biot-Soleil double plate, anisotropic substances producing different tints in the two halves of the field. The axial directions may be determined in this way.

Austenite in steels is isotropic, but martensite anisotropic. The carbide in iron and steel from 0 to 4·2% of carbon has identical properties. The compound Ag_2Al is anisotropic. C. H. D.

Thermal Analysis of Mixtures of Alkali Hydroxides with the Corresponding Halogen Salts. I. Potassium Compounds GIUSEPPE SCARPA (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 738—746).—Thermal measurements of the systems KOH–KF, KOH–KCl, KOH–KBr, and KOH–KI were carried out in an atmosphere of nitrogen and in silver crucibles, temperatures being determined by means of a silver-nickel couple; with a few mixtures, rich in potassium fluoride, a platinum crucible and a platinum : platinum-rhodium couple were used.

Potassium hydroxide has m. p. 380°, and the transformation point 260°. Hevesy (A., 1910, ii, 835) gave m. p. 360° and transformation point 248°, and Neumann and Bergve (A., 1914, ii, 422), m. p. 345°. Potassium fluoride solidifies at 857°; Plato (A., 1907, ii, 239) gave 859·9°; Karandezen (*Zbl. Min. Geol.*, 1909, 728), 867°; Kurnakov and Schemtschuschni (A., 1906, ii, 443), 837°; and Puschin and Baskov (A., 1913, ii, 319), 885°. The solidifying points of all mixtures of potassium hydroxide and fluoride lie between those of the components, which are perfectly miscible in the solid state, with formation of mixed crystals of only one kind. The transformation point of the hydroxide is gradually lowered by increase in the proportion of fluoride.

Potassium chloride has m. p. 776°. Hüttner and Tammann (A., 1905, ii, 229) gave 778°; Menge (A., 1911, ii, 982), 776°; Truthe (A., 1912, i, 612), 775°; Sandonnini (A., 1911, ii, 606), 776°; Kurnakov and Schemtschuschni (*loc. cit.*), 790°; and Ruff and Plato (A., 1903, ii, 588), 790°. Potassium bromide has m. p. 760°. Ruff and Plato (*loc. cit.*) gave 750°; Kurnakov and Schemtschuschni (*loc. cit.*), 757°; Hüttner and Tammann (*loc. cit.*), 740°; Amadori (A., 1912, ii, 154), 740°; and de Cesaris (A., 1911, ii, 804), 730°. The systems KOH–KCl and KOH–KBr form solid solutions of two kinds with a miscibility gap, corresponding with Roozeboom's type IV.

Potassium iodide has m. p. 695°. Ruff and Plato (*loc. cit.*) gave 705°; Kurnakov and Schemtschuschni (*loc. cit.*), 693°; and Hüttner and Tammann (*loc. cit.*), 680°. The curve of primary crystallisation of the system KOH–KI consists of two branches, which descend from the melting points of the components and

meet at the eutectic point 250°, corresponding with about 73 mol. % KOH. T. H. P.

Acid Sodium Borates. J. Ponomarev (*Zeitsch. anorg. Chem.*, 1914, **89**, 383—392).—Mixtures of borax and boron trioxide are fused, and exposed to a temperature-gradient in a platinum boat according to Tammann's method for examining spontaneous crystallisation (A., 1914, ii, 545). After the limit of crystalline growth has been reached, a new reading is obtained by drawing the boat slightly into the furnace, so that a part of the crystals melts. A new boundary is then obtained with greater accuracy than the first.

The results prove the existence of two definite borates containing more boron trioxide than ordinary borax, namely, $Na_2O,3B_2O_3$ and $Na_2O,4B_2O_3$, melting at 694° and 783° respectively. Ordinary borax melts at 730°. The acid borates crystallise without appreciably altering the composition of the glassy mass. The habit, but not the optical properties, of the crystals changes with the composition. There thus appears to be a continuous series of solid solutions from $Na_2O,2B_2O_3$ to $Na_2O,4B_2O_3$, and somewhat further. It is possible by this means to obtain crystallisation in mixtures which contain as little as 3% Na_2O. C. H. D.

Borates. The System Na_2O-B_2O_3-H_2O at 60°. I. U. Sborgi and F. Mecacci (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 443—448. Compare A., 1913, ii, 213, 318, 700, 775; 1914, ii, 562, 648).—This system, which was investigated by Dukelski (A., 1906, ii, 610) at 30°, has been studied by the authors at 60° over that part of the diagram where the solid phase lies between boric acid and the metaborate. After boric acid, the stable phase consists of the decahydrated pentaborate, 1 : 5 : 10, and then of the pentahydrated borate, 1 : 2 : 5. T. H. P.

Action of Hauerite on Silver and Copper. E. Quercigh (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 626—631).—According to Beutell (A., 1914, ii, 136), the action of hauerite on silver and copper at the ordinary temperature, observed by Strüver (A., 1901, ii, 317), does not consist in an interaction of the solid mineral and metal, but is produced by the vapour of the sulphur resulting from the decomposition of the hauerite in the air. This explanation may hold to some extent, but the author finds that the action proceeds when the metal and mineral are pressed together under toluene. Experiment shows that the action is due neither to the presence of free sulphur or hydrogen sulphide in the hauerite, nor to removal of sulphur from the mineral by the toluene. These results confirm the interpretation of the phenomenon advanced by Strüver, namely, that the combined sulphur of the hauerite passes to the copper or silver with which the mineral is in contact. T. H. P.

The Peroxides of the Alkaline Earths I. E. H. Riesenfeld and W. Nottebohm (*Zeitsch. anorg. Chem.*, 1914, **89**, 405—412).—The

preparation of barium peroxide in the wet way always yields the octahydrate when more than 1 mol. $Ba(OH)_2$ is present per mol. H_2O_2. Above 60° it is formed, whatever the composition of the solution. The anhydrous peroxide cannot be obtained from aqueous solution. Below 40°, the diperoxyhydrate, $BaO_2,2H_2O_2$, is obtained from solutions containing much hydrogen peroxide. A compound, BaO_2,H_2O_2, may also be obtained between 30° and 60°.

Anhydrous strontium peroxide is obtained from very concentrated solutions above 50°, otherwise the octahydrate is formed. The diperoxyhydrate has not been obtained by direct precipitation, but only by the action of concentrated hydrogen peroxide on the octahydrate at low temperatures.

Calcium peroxide separates in the anhydrous form from very concentrated solutions near 0°, and above 40° even from very dilute solutions. The octahydrate is obtained from dilute solutions at ordinary temperatures. A dihydrate may be prepared from the anhydrous compound. The diperoxyhydrate resembles that of strontium.

Water slowly converts all the compounds into the octahydrates.

C. H. D.

Peroxides of the Alkaline Earths. II. The Thermal Formation of Calcium Peroxide. E. H. Riesenfeld and W. Nottebohm (*Zeitsch. anorg. Chem.*, 1914, **90**, 371—376. Compare Bergius, A., 1912, ii, 1171).—Calcium peroxide octahydrate (preceding abstract) is dehydrated at 100°, and then heated for definite periods at different constant temperatures. There is no appreciable decomposition below 220°. Up to 273° decomposition is slow, but then becomes rapid. Finely divided calcium peroxide decomposes explosively at 275° when rapidly heated. The dissociation pressure of calcium peroxide at 255° is more than 190 atmospheres, the pressure employed in the experiments in a closed apparatus. A calculation from Nernst's formula gives the approximate value of 1000 atmospheres. The absorption of oxygen observed by Bergius must be attributed to the formation of potassium peroxide from the mixture used. C. H. D.

The Hydration of Calcium Sulphate Hemihydrate. Paul Rohland (*Zeitsch. anorg. Chem.*, 1914, **89**, 352—354).—Substances, which increase the solubility of the hemihydrate accelerate its hydration, whilst substances which diminish its solubility retard hydration. Many salts are classified according to this distinction. The equilibrium to be considered is that between ionised and unionised calcium sulphate, dissolved dihydrate, and solid hemihydrate and dihydrate. C. H. D.

The Dehydration Products of Gypsum. R. Grengg (*Zeitsch. anorg. Chem.*, 1914, **90**, 327—360).—The hemihydrate $CaSO_4,\frac{1}{2}H_2O$, prepared by digesting gypsum with warm nitric acid, forms hexagonal prisms. Larger crystals are obtained by heating gypsum with concentrated sodium chloride solution at 80—100°. The hexagonal form is only apparent, optical investi-

gation showing that the crystals are rhombic, but repeatedly twinned. Water attacks the prisms chiefly at the middle and the ends. Gentle heating in paraffin increases the double refraction without alteration of external form, soluble anhydrite being formed. Near 360° the crystals change into insoluble anhydrite, which is still rhombic, but arranged in parallel fibres, giving the appearance of optically uniaxial crystals. On heating to bright redness, the crystals become turbid, being ultimately converted into glass, containing particles of calcium oxide.

The formation of hemihydrate on heating gypsum appears to take place through the stage of soluble anhydrite, which then reabsorbs water vapour. Natural anhydrite is identical with the artificial insoluble modification, the greater reactivity of the latter being due to its fibrous structure.

Microscopical examination of clear cleavage plates of gypsum shows that conversion into the hemihydrate takes place along lines parallel to the *c*-axis. More perfect pseudomorphs are obtained by heating in paraffin or with water in an autoclave, the water being allowed to escape under pressure at the end of the experiment to prevent reconversion into gypsum. The fibrous hemihydrate does not set well with water, although hydration takes place readily as the outer crystalline form is retained. In this way, pseudomorphs of gypsum after gypsum, through hemihydrate, are formed.

The so-called Estrich plaster consists of anhydrite and calcium oxide in solid solution, partly crystalline and partly glassy.

The microscopical methods of distinguishing the different technical products are described. C. H. D.

Solubility of Calcium Carbonate and Magnesium Carbonate in Water Free from Carbon Dioxide as Affected by the Presence of Mineral Salts and Organic Substances. F. Gothe (*Chem. Zeit.*, 1915, **39**, 305—307; 326—327).—The solubility of calcium carbonate in water free from carbon dioxide varies within narrow limits, the average quantity being 31·0 mg. per litre. Magnesium carbonate shows greater variations, but the average quantity dissolved is 94·4 mg. per litre. The solubility of both calcium carbonate and magnesium carbonate is increased by the presence of chlorides, nitrates, and sulphates in the water, but decreased by alkali carbonates, and by the chlorides, nitrates, and sulphates of the alkali earths. Ammonium salts decompose the two carbonates in question, and the effect on the solubility cannot be determined. The solubility is increased when the water contains organic (humus) substances, especially when alkali salts are also present, but is decreased in the presence of alkali-earth salts. W. P. S.

Conductivity Study of the Reaction between Calcium Nitrate and Dipotassium Hydrogen Phosphate in Dilute Solution. W. A. Withers and Alex. L. Feild (*J. Amer. Chem. Soc.*, 1915, **37**, 1091—1105).—It is well known that the reaction

between a soluble calcium salt and dipotassium hydrogen phosphate in presence of excess of ammonia results in the precipitation of tricalcium phosphate, but with regard to the reaction which takes place in the absence of ammonia there is considerable divergence of opinion.

A study has now been made by means of conductivity measurements to determine the changes which occur when calcium nitrate (in quantities equivalent to 0—500 mg. of nitrogen) is added in increasing amounts to a solution of dipotassium hydrogen phosphate (1 gram per litre), and the results have been verified by analysis of the liquid phase.

A break occurs in the conductivity curve when calcium nitrate, to the amount of 120 mg. of nitrogen, has been added per litre, and when equilibrium is reached (at the end of forty-eight hours) the reaction is represented by the equation (1)

$$4K_2HPO_4 + 3Ca(NO_3)_2 = Ca_3(PO_4)_2 + 2KH_2PO_4 + 6KNO_3.$$

Soon after mixing, however, the following reaction probably occurs, (2) $4K_2HPO_4 + 4Ca(NO_3)_2 = Ca_3(PO_4)_2 + Ca(H_2PO_4)_2 + 8KNO_3$. This is an unstable condition, and persists for only a few minutes. A further change then takes place until the stable condition shown by equation (1) is established. If excess of calcium nitrate is employed, the unstable condition is either not produced or else persists for an exceedingly short time, the stable condition being attained immediately.

The liquid phase of a number of mixtures was analysed at the end of forty-eight hours by a method of conductivity titration. The amount of the dihydrogen phosphate was estimated by means of the break in the conductivity curve obtained on adding increasing quantities of dilute potassium hydroxide, and the amount of the monohydrogen phosphate by means of a similar break obtained on adding increasing quantities of dilute nitric acid. The results confirmed the reaction expressed by equation (1). The deviation of the observed values of the monohydrogen phosphate from the theoretical shows that the precipitated tricalcium phosphate undergoes partial hydrolysis in such a way as to appear in the liquid phase as the monohydrogen phosphate. The extent of this hydrolysis is roughly proportional to the concentration of the dihydrogen phosphate present, and is slightly diminished by excess of calcium nitrate. E. G.

Solubility of the Different Constituents of Basic Slag. Sirot, Maurice, and Joret (*Biol. Zentr.*, 1915, **44**, 150—151; *J. d'Agric. prat.*, 1914, **78**, i, 78).—The silica, phosphoric acid, calcium, magnesium, iron, manganese, and sulphuric acid present in basic slag are all soluble in various dilute acids, the amounts dissolved varying with the fineness of the slag and with different acids, citric and malic acids dissolving the most, then lactic, acetic, tartaric, and oxalic acids. About 90% of the total silica is dissolved by citric, lactic, and malic acids. The variations in the

solubility of other constituents were: P_2O_5, 24—87·2; CaO, 48·8—89·4; MgO, 3·1—67·6; Fe, 10·8—41·4; and Mn, 7·7—39·7%.
N. H. J. M.

The Compound $8CaO,Al_2O_3,2SiO_2$, the Chief Constituent (Alite) of Portland Cement Clinker. Ernst Jänecke (*Zeitsch. anorg. Chem.*, 1914, **89**, 355—369).—Further evidence is brought for the view (A., 1912, ii, 159, 450, 761) that alite consists of a definite ternary compound, $8CaO,Al_2O_3,2SiO_2$, which is supported by thermal and microscopical evidence. Mixtures of pure silica, alumina, and calcium carbonate are fused by an electric arc, using a hollow plate of dynamidone (strongly ignited alumina). A solid cake is obtained, separated from the plate by a layer of unmelted powder. The product is very finely ground, and fused in a platinum crucible in a carbon tube furnace in an atmosphere of nitrogen. Cooling curves are taken simultaneously by readings of a millivoltmeter and autographic records of a mirror galvanometer. Five mixtures in the neighbourhood of the compound have been examined. The mixture corresponding exactly with the compound has the highest freezing point, 1385°, and the sharpness of the arrests on the cooling curves does not suggest the formation of solid solutions. The eutectic points are probably very near to the maximum.

The compound forms needles, probably monoclinic, with refractive index 1·63, weak double refraction, D 3·035, and hardness nearly 7. Photographs in colours are given to prove its identity with the alite of clinker. The failure of other workers to obtain a homogeneous product is due to insufficient heating, a temperature much above the actual melting point being required, on account of the great viscosity. The difference between the composition of the compound and that of normal clinker is due to the fact that the latter is not in equilibrium, owing to an insufficiently high temperature (compare Rankin and Wright, this vol., ii, 50).
C. H. D.

The Window-glasses of the Middle Ages. G. Chesneau (*Compt. rend.*, 1915, **160**, 622—624).—The author has analysed fragments of violet, blue, green, and red glass detached from the rose window of Rheims Cathedral, and dating back to the end of the thirteenth century. The results for each colour are set out in detail, and attention is drawn to the probable origin of the metallic colouring matters used in each case. All the four glasses have approximately the same content in respect to silica and the oxides of aluminium and magnesium, the violet and green glasses having, however, a rather high percentage of potassium oxide.
W. G.

Magnesium Amalgams. L. Cambi and G. Speroni (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 734—738).—Using the apparatus employed with calcium amalgams (*ibid.*, 1914, [v], **23**, ii, 599), the authors have carried out a thermal investigation of magnesium

amalgams in an atmosphere of dry carbon dioxide, the proportion of magnesium varying from 0 to 1 Mg : 1 Hg. The results demonstrate the formation of the *compound* $MgHg_2$, m. p. 168° (decomp.), and indicate also the existence of the compound MgHg, but this requires confirmation. At 280°, the solubility of magnesium in mercury is 3·88%, whereas Kerp, Böttger and Iggena (A., 1900, ii, 656) gave the solubility as about 1% at 300°. The solubility of magnesium, 10 atom. % at 106°, is greater than that of calcium, 2·86 atom. % at 109° (*loc. cit.*). Saturated calcium amalgam, b. p. 377°, contains 13—14 atom. % Ca, whilst saturated magnesium amalgam, b. p. 415°, contains 32—34 atom. % Mg. The existence of the compounds $MgHg_6$ (Kerp, Böttger and Iggena, *loc. cit.*) and $MgHg_4$ (Bachmetjev and Wsharov, *Jahresb.*, 1893, 108) is not confirmed by thermal analysis. T. H. P.

Constitution of Hydrates: Dehydration of Magnesium Sulphate Heptahydrate. A. Johnsen (*Centr. Min.*, 1915, 289—292).—In a dry atmosphere at the ordinary temperature, magnesium sulphate ($MgSO_4,7H_2O$) slowly and gradually loses one molecule of water; over calcium chloride at $14\pm1°$ the loss is 1·01 mol. in twelve days, and at $11\pm1°$ it is 0·98 mol. in twenty-one days. The partly dehydrated dextrorotatory crystals have no inoculating influence on a metastable solution of magnesium sulphate. The formula of the salt may be written

$$[Mg(H_2O)_6]SO_4,H_2O,$$

or perhaps $[Mg(H_4O_2)_3]SO_4,H_2O$ or $[Mg(H_6O_3)_2]SO_4,H_2O$.

L. J. S.

Zinc Peroxide. E. H. Riesenfeld and W. Nottebohm (*Zeitsch. anorg. Chem.*, 1914, **90**, 150—152. Compare Kuriloff, A., 1904, ii, 36; Ebler and Krause, A., 1911, ii, 801).—By adding hydrogen peroxide to an ammoniacal solution of zinc nitrate at −5°, a white, amorphous precipitate is obtained, which gives the ratio ZnO : active oxygen : water = 1 : 0·84 : 0·71 after drying. By stirring with concentrated hydrogen peroxide, this ratio may be increased to 1 : 0·91 : 0·87, indicating the presence of ZnO_2.

C. H. D.

The Nature of Subsidiary Valencies. XI. Ammines of Zinc. Fritz Ephraim and Edouard Bolle (*Ber.*, 1915, **48**, 638—648).—From what has been said in the ninth paper (this vol., ii, 441), it follows that the stability of ammines, $[M(NH_3)_n]X_2$, depends, not only on the influence of the metal, but also on that of the central atom in the anion, which influences oppose each other. The stability of the whole molecule is, therefore, the resultant of the two influences, and, consequently, it may appear that there is no parallelism between analogous compounds. Thus, the temperature of decomposition of the hexammines (or pentammines) of nickel salts decreases in the order ClO_4, I, Br, ClO_3, NO_3, S_2O_6, Cl, SO_4, S_2O_3, S_4O_6, NO_2, H_2PO_2, HCO_2, CNS, $CH_3{\cdot}CO_2$ (A., 1913, ii, 1061), whilst the order in the case of zinc is S_2O_6, I,

Br, Cl, S_4O_6, S_2O_3, HCO_2, ClO_4, SO_4, NO_3, C_2O_4, ClO_3, CNS, $C_6H_5{\cdot}CO_2$, $CH_3{\cdot}CO_2$, and NO_2.

The series of zincammine salts is increased by the following new members.

By saturating a concentrated solution of zinc nitrate with ammonia, under water cooling, a crystalline *tetrammine*, $Zn(NO_3)_2,4NH_3$, separated, which changed into a *hexammine* when treated with more ammonia at 0°. A solution of zinc thiosulphate gave a *triammine* which, in the dry state, absorbed more ammonia and gave a *pentammine*. A solution of zinc dithionate gave a *tetrammine hydrate*, $ZnS_2O_6,4NH_3,H_2O$, which lost water at 95° in a current of ammonia, and then, at the ordinary temperature, gave a *pentammine*. A solution of zinc tetrathionate (prepared by the action of iodine on the thiosulphate) gave a *triammine*, $ZnS_4O_6,3NH_3$, and this, in the dry state, a *pentammine*. Zinc sulphite solution deposited a *triammine*. Zinc perchlorate solution gave a tetrammine, and this solid a *hexammine*,

$$Zn(ClO_4)_2,6NH_3.$$

Zinc nitrite gave a doubtful *monoammine*. Anhydrous zinc formate yielded a *pentammine*; anhydrous zinc acetate, obtained by drying at 150° and extracting the product with glacial acetic acid in a Soxhlet tube, formed a *diammine*; zinc oxalate, dried at 140°, gave a *pentammine*; anhydrous zinc benzoate formed a *tetrammine* at the ordinary temperature, and a hexammine at 0°. Zinc thicyanate solution yielded a *diammine* which, when dry, gave a *tetrammine* at the room temperature and a *hexammine* at 0°.

These, with the chlorate tetrammine and hexammine (this vol., ii, 167), the sulphate tetrammine (A., 1913, ii, 496), and the hexammines of the haloids (*ibid.*, 129), are tabulated in order of stability, with the absolute temperatures of dissociation and the heats of formation, calculated from Nernst's formula.

[SUPPLEMENT.]—The ammines which are most nearly related in stability to those of zinc are the copper compounds. To the tension measurements of the copper haloid hexammines (A., 1913, ii, 129) are now added those of copper tetrammine acetate and copper pentammine oxalate (Horn, A., 1906, ii, 231; 1908, i, 121).

J. C. W.

Revision of the Atomic Weight of Lead. II. Analysis of Lead Bromide. GREGORY PAUL BAXTER and THORBERGUR THORVALDSON (*J. Amer. Chem. Soc.*, 1915, **37**, 1020—1027).—Baxter and Wilson (A., 1908, ii, 281) determined the atomic weight of lead by the analysis of lead chloride, and obtained the value 207·09 (Ag=107·880). An account is now given of determinations made by the analysis of lead bromide.

Lead bromide was precipitated by adding hydrobromic acid to solution of lead nitrate, and crystallised by dissolving it in hot concentrated hydrobromic acid and diluting the solution with water. The salt was dried by fusing it in a current of nitrogen and hydrogen bromide. It was found that lead bromide prepared

in this way did not yield a clear solution, owing to the separation of a small quantity of basic bromide. As it was probable that the fused bromide itself is not basic, the solutions for analysis were made with dilute acetic acid. In this case, however, a slight, black, insoluble residue was always obtained, which consisted of carbon and silica, and probably amounted to about 0·004%. Weighed amounts of the salt were dissolved in hot water, acidified with acetic acid, and, when cold, the solutions were treated with a solution of a weighed, nearly equivalent, quantity of silver. The deficiency of bromide or silver was then added in the form of very dilute standard solutions, so that the exact amount of silver required could be accurately estimated. The silver bromide was collected and weighed.

From the ratios $PbBr_2$: 2Ag and $PbBr_2$: 2AgBr, the average value of the atomic weight obtained was in each case 207·19 (Ag = 107·880; Br = 79·916). E. G.

Revision of the Atomic Weight of Lead. III. Analysis of Lead Bromide and Chloride. Gregory Paul Baxter and Fred Leslie Grover (*J. Amer. Chem. Soc.*, 1915, **37**, 1027—1061).—In view of the discrepancy between the values found for the atomic weight of lead by Baxter and Wilson (A., 1908, ii, 281) and Baxter and Thorvaldson (preceding abstract), it seemed possible that specimens of lead from different sources might not be identical, and in connexion with the theory of atomic disintegration of the radioactive elements, a knowledge of the exact value of the atomic weight has acquired considerable importance. Eleven specimens of lead salts from various geographical and mineralogical sources were therefore purified and examined, both spectroscopically and also by the analysis of the chloride and bromide. None of these specimens was appreciably radioactive, and no evidence of any dissimilarity could be obtained.

It has been found that lead can be freed from small quantities of silver and copper by the recrystallisation of the nitrate, but that electrolytic deposition with a dissolving anode through nitrate or chloride electrolyte does not give satisfactory results.

Lead bromide and chloride which have been fused in an atmosphere of the corresponding hydrogen haloid are neutral, but undergo hydrolysis in water, with precipitation of basic salts. Lead chloride crystallised from water is basic, but if crystallised from very dilute hydrochloric acid it is neutral.

The analyses were carried out by a similar method to that used by Baxter and Thorvaldson, and the following values of the atomic weight were obtained. From the ratio $PbBr_2$: 2Ag, 207·20; from $PbBr_2$: 2AgBr, 207·18; from $PbCl_2$: 2Ag, 207·21; and from $PbCl_2$: 2AgCl, 207·22. The average value for the atomic weight of lead was thus found to be 207·20 (Ag = 107·880; Br = 79·916; Cl = 35·457). E. G.

Physico-chemical Studies on Lead. II. Ernst Cohen and W. D. Helderman (*Zeitsch. physikal. Chem.*, 1915, **89**, 733—741. Compare *ibid.*, 1910, **74**, 202).—Pure lead which contains not more

than 0·001% copper and 0·0006% iron has been used in density determinations. As a mean of six determinations, the value of D_4^{25} is found to be 11·3299. It is found that when pure lead is suspended in a 40% solution of lead acetate which contains 100 c.c. of 1·16 nitric acid per litre, in a few days the appearance of the metal changes. The change is such that small ridges appear, which indicate that the metal has contracted. No evolution of gas takes place, so that the change is a physical one, and not a chemical one. The density of the changed lead has been determined with the product formed at 15°, 50°, and 25°. The following mean values were obtained: 11·3415, 11·3129, and 11·3283. Dilatometric measurements have also been carried out, which, taken with the density of the product produced at different temperatures, lead to the view that the changed lead is made up of several allotropic forms. J. F. S.

The Higher Oxides of Lead and Their Dissociation. W. Reinders and L. Hamburger (*Zeitsch. anorg. Chem.*, 1914, **89**, 71—96).—The lead oxide is placed in a porcelain boat, contained in a hard glass tube connected by a ground joint with the manometer, pump, and oxygen reservoir. The temperature of the electric furnace is kept constant within 0·2% by shunting a part of the current through a regulator. The latter is a heating coil immersed in the bulb of a toluene regulator, which is enclosed in an air jacket and immersed in a constant-temperature water-bath. The regulator is maintained at a temperature 75° above that of the bath, and its mercury column, by rising or falling, inserts or cuts out a resistance in the main circuit, an electromagnet being used.

The active oxygen is estimated by distillation with hydrochloric acid in an apparatus with ground joints, a current of carbon dioxide being passed through during the operation. As a control, the oxide is mixed with a measured quantity of 0·2*N*-oxalic acid, boiled with nitric acid, and titrated hot with permanganate.

Red lead, purified by repeated heating with lead nitrate or acetate solution, only reaches equilibrium slowly when dissociating. The $p-t$ curve from 445° to 607° is quite smooth, and there is no evidence of a solid solution of PbO and Pb_3O_4, or of any intermediate compound. The monoxide prepared in this way is yellow, with a greenish shade when obtained at high temperatures. The same pressures are obtained by admitting oxygen to lead oxide which has been prepared by complete decomposition of red lead in a vacuum. The red monoxide prepared in the wet way only absorbs oxygen very slowly at 540°, and retains its colour. The reactivity varies with the mode of preparation. The heat of formation of red lead is calculated, and an expression is found for its dissociation.

The dissociation of lead peroxide gives unstable products down to $PbO_{1·36}$ at 361°. Red lead is not formed, but the products are solid solutions of varying composition, unstable in regard to red lead. The wet methods of preparing pure red lead from the

peroxide (Milbauer, A., 1914, ii, 464) depend on the use of catalysts to obtain equilibrium.

The solid solutions are brown to olive-green. The limit is reached at $PbO_{1\cdot36}$, beyond which litharge appears as a new phase. The formation of definite oxides other than Pb_3O_4, such as Pb_2O_3, Pb_5O_7, or Pb_5O_8, has not been confirmed. C. H. D.

The System Lead Oxide–Copper Oxide. J. C. J. CUNNINGHAM (*Zeitsch. anorg. Chem.*, 1914, **89**, 48—52).—The oxides are heated together in a platinum crucible in an electric furnace, the temperature not being raised above 980°, in order to avoid formation of cuprous oxide. Lead oxide melts at 875°, and the eutectic point is at 698° and 30% or more of cupric oxide. The ascending branch of the curve could not be determined. Evidence of a compound has not been found. C. H. D.

Properties of Thallium–Lead Alloys. LUIGI ROLLA (*Gazzetta*, 1915, **45**, i, 185—191).—The investigations of Kurnakov have shown that, in certain cases, a maximum occurs on the melting-point diagram of a binary system without corresponding singular points on the curves representing other physical properties. Thus, with lead-thallium alloys, the fusion diagram exhibits a maximum (compare Kurnakov and Pushin, A., 1907, ii, 262), and the curve of electrical conductivity at 25° is continuous and shows a minimum, but this is not in correspondence with the maximal melting point. Similar behaviour is shown by the hardness curve, and the conclusion is drawn that lead-thallium alloys are composed of solid solutions.

According to Bernouilli's experiments (A., 1910, ii, 1030; 1911, ii, 363), a dilute solution of two metals is thermoelectrically negative towards the metallic solvent, that is, behaves in the same way as bismuth does towards other metals. Further, as the concentration of the alloy increases, the thermoelectric force also increases, the behaviour of the solid solution towards the solvent becoming increasingly similar to that of bismuth. Since, according to Schenck's theory, $\epsilon = k \ln (p_1/p_2)$, where ϵ is the thermoelectric force for a difference in temperature of 1°, k a constant, and p_1 and p_2 the pressures of the electrons in the alloy and the metallic solvent, and since also Bernouilli's results indicate that p_1 is less than p_2, it would appear that Babo's law may be extended to electronic phenomena.

Thallium-lead alloys exhibit singularity in this respect, the β-solid phase, at least until the percentage of thallium is moderately small, being thermoelectrically positive towards lead. Consequently, if these alloys are regarded as solid solutions, Babo's law is not verified, a change of sign being necessary in Schenck's formula. From the Einstein-Planck and the Nernst-Lindemann formulæ, Bernouilli has deduced the relation $\epsilon = K \log (T_f' / T_f)$, where T_f' and T_f are the absolute melting points of the alloy and pure solvent respectively. As with Bernouilli's alloys, so in the present case, T_f' is greater than T_f, and ϵ consequently greater than zero.

Lewkonja (A., 1907, ii, 261) regards the lead-thallium alloy of maximum melting point as the definite compound $PbTl_2$, and if this has real existence, its formation from the components should be accompanied by a variation in volume. The author finds, however, that the specific volume of an alloy of this composition is in agreement with the value calculated by the law of mixtures. The same is the case with the specific heat, but here the modern theory of specific heats indicates that the difference between the observed and calculated values should be small. The heat of formation of the alloy, $Pb : Tl_2$, is 6608 cal. T. H. P.

Cuprous Carbonate. P. CARLES (*Bull. Soc. chim.*, 1915, [iv], **17**, 163—164).—In the ordinary process for the manufacture of cupram spray fluid by the action of air and liquid ammonia, the copper becomes coated after a time with copper carbonate, and the action ceases. A piece of copper thus coated was left in contact with the ammonia under observation. The blue colour of the surface passed spontaneously to green, and then slowly to reddish-yellow, which remained permanent. This material was detached by boiling water, and shown to be *cuprous carbonate*, produced by the reducing action of the copper. It is a glaucous, green powder insoluble in water and ammonia, giving the ordinary carbonate reactions. With nitric acid, oxides of nitrogen are evolved, and a pale blue solution left. W. G.

Method of Determining the Hydrates Formed by a Salt. H. W. FOOTE (*J. Amer. Chem. Soc.*, 1915, **37**, 1200—1201).—In the author's paper on hydrates of copper sulphate (this vol., ii, 97), the work of Bell and Taber (A., 1908, ii, 382) was overlooked. It is now shown that both investigations demonstrate the existence of the same hydrates under similar conditions. E. G.

Action of Halogens on Mercuric Sulphate. CHATEAU (*Bull. Soc. chim.*, 1915, [iv], **17**, 121—124).—The author has repeated Brückner's work on the action of iodine on mercuric sulphate in the presence of water (compare A., 1906, ii, 613). He confirms his results, but considers that the product, rather than being a single substance, is an equilibrium mixture of three salts, basic mercuric sulphate, mercuric iodosulphate, and mercuric iodate in the proportion $6(HgSO_4,HgO)$, $6(HgSO_4,HgI_2)$, HgI_2O_6. He has replaced the iodine in turn by bromine and chlorine in this reaction, but finds that the product in these cases is mercuric bromide and mercuric chloride, respectively, oxygen being evolved. W. G.

Preparation of Aluminium from Russian Minerals. N. PUSCHIN, E. DISCHLER, and M. MAKSIMENKO (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1347—1365).—When a current density of 2—3 amperes per sq. cm. of the anode surface, and a fused mixture containing about 40 mol. % of aluminium fluoride, are employed, and alumina is periodically added to the mixture, the extraction of aluminium

may be carried on continuously for a long time, the yield approximating to that obtained in large industrial plant. Aluminium may be prepared from the simonite found in the Urals, the mineral being converted first into the oxide and then into the oxyfluoride, Al_2OF_4, which is found to be more suitable than the fluoride for treatment in the electric furnace. T. H. P.

Present Position of the Investigation of Ultramarine. LAURENZ BOCK (*Zeitsch. angew. Chem.*, 1915, **28**, 147—152).—Largely a summary of the already published results of various investigators in this field. The experiments of Singer (*Diss.*, Berlin, 1910) on the formation of ultramarine-green from artificial sodium aluminium silicates of the type $Na_2O,Al_2O_3,2SiO_2,2H_2O$, by the replacement of the water of crystallisation by sulphides, throw considerable light on the reactions occurring in the ultramarine fusion. At 150—360° the resin and sulphur act on the sodium sulphate and carbonate, respectively, with the formation of fused sulphides and polysulphides, which at 500° and upwards react with the kaolin with formation of the intermediate product, ultramarine-green, which, on the basis of a silicate mixture of the composition $Al_2O_3,3SiO_2$, may be represented by the structure

$$\begin{matrix}NaS\\NaO\end{matrix}\!\!>\!Al\cdot O\cdot SiO\cdot O\cdot Si(ONa)_2\cdot O\cdot SiO\cdot O\cdot Al\!<\!\begin{matrix}SNa\\ONa\end{matrix}$$

This substance is only obtained by the complete exclusion of air, otherwise, as in technical practice, oxidation to ultramarine-blue sets in, which substance no longer loses the whole of its sulphur on treatment with acids, as does ultramarine-green, and in which, therefore, the presence of ·SONa groups is postulated. In the formation of ultramarine-violet by the action of chlorine and hydrochloric acid on the blue, these groups are converted into $\cdot NaS_2O_3$ (compare Wunder, A., 1913, ii, 54, 221, 864). The author considers that ultramarines with a high percentage of alumina are mainly aluminate-silicates, whilst with increasing silicon content the constitution approximates more to that of aluminium double silicates, or, in other words, the NaO-, NaS-groups are then mainly attached to silicon. Constitutional formulæ are suggested for the various ultramarine compounds. G. F. M.

Artificial Sillimanite. W. EITEL (*Zeitsch. anorg. Chem.*, 1914, **88**, 173—184. Compare Shepherd, Rankin and Wright, A., 1909, ii, 1015).—Artificial sillimanite may be prepared by firing a mixture of iron oxide thermite with silica. A part of the silica is volatilised, so that an analysis of the product is necessary. The mass is completely crystalline, and contains many gas cavities. Much of the sillimanite is in the fibrous form known as fibrolite, but crystals 2—3 mm. by 0·15—0·2 mm. are also found. Only the prism faces are well developed. When separated from the accompanying corundum by methylene iodide and bromoform, the sillimanite has D 3·10—3·15, Shepherd and Rankin having found 3·03, whilst the natural mineral has D 3·20—3·25. The refraction

and dispersion have also been measured. The angle between the optical axes $2E$ diminishes rapidly with increasing temperature, whilst that of the natural crystals increases slightly. The difference may be due to the presence of iron. Metallic iron and oxides are present, representing 6·34% FeO. Corundum does not appear to retain sillimanite in solid solution. C. H. D.

Investigations at High Temperatures. V. Manganese and Carbon. Otto Ruff and Walter Bormann (*Zeitsch. anorg. Chem.*, 1914, **88**, 365—385. Compare A., 1912, ii, 1176; 1913, ii, 325).—The carbon resistance vacuum furnace (A., 1914, ii, 336) is used. Temperatures up to 1500° are measured by means of a thermocouple, above that by a Wanner pyrometer. The solubility of carbon in the metal is determined by keeping for a definite time at constant temperature in a graphite crucible and quenching. The boiling point of the metal saturated with carbon is determined by direct observation, and that of the pure metal in the same manner, using a zirconia crucible in place of graphite. The composition of the vapour is found by determining the loss of metal and carbon by volatilisation, the crucible being covered by two perforated discs to prevent loss by spitting.

The solubility of carbon in manganese increases slowly from 1360° to 1525°, the boiling point of the solution under 30 mm. pressure. It is then 7·12%. Pure manganese boils at 1510° under the same pressure, and the vapour of the mixture contains 1·94% of carbon. The whole of the carbon in the rapidly cooled alloys is present in the combined state. The residue, after distillation of the manganese, contains free graphite. The existence at higher temperatures of a carbide richer in carbon than Mn_3C is probable. C. H. D.

New Method of Preparation and Some Interesting Transformations of Colloidal Manganese Dioxide. Edgar J. Witzemann (*J. Amer. Chem. Soc.*, 1915, **37**, 1079—1091).—Colloidal manganese dioxide can be readily obtained by the action of potassium permanganate on a solution of dextrose, lævulose, or galactose in dilute alkali hydroxide; when formed under these conditions, it first passes into a viscous or gel stage, and subsequently into a limpid, colloidal solution. The properties of the first stage are those of a typical emulsoid, and those of the later stage of a suspensoid. The transformations of the emulsoid are typical and normal, except for a slower and simultaneous transformation into a suspensoid, owing to the effect of the alkali hydroxide in accordance with the generalisations of Mayer, Schaeffer, and Terroine (A., 1908, ii, 24, 264). Both transformations are readily affected by variations in the temperature, concentration of the reacting mixture, and concentration of the alkali hydroxide. The colloid is best formed at low temperatures, and the concentrated colloid is readily coagulated on warming. Relationships are suggested between the properties of manganese in biochemical reactions and the properties of colloidal manganese dioxide. E. G.

Sulphides of Manganese. V. M. Fischer (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1481—1519).—Many contradictory statements have been made with reference to the various modifications of manganese sulphide and the methods of obtaining them, practically the sole point of agreement being that the action of potassium or sodium sulphide on a manganous salt yields the rose-coloured manganous sulphide, and never the green form.

The methods given in the text-books for preparing the green sulphide rarely give positive results, but the following procedure is invariably successful. Ten grams of tetrahydrated manganous chloride or a corresponding quantity of the sulphate are dissolved, together with 5 grams of ammonium chloride, in 25 c.c. of water in an Erlenmeyer flask, 100 c.c. of 25—29% ammonia solution being then added. From the clear solution thus obtained, the rose-coloured manganese sulphide is precipitated by gradual addition from a dropping funnel of 100 c.c. of cold ammonium hydrogen sulphide, prepared by saturating 2·5% ammonia solution with hydrogen sulphide; during the precipitation, the liquid is constantly shaken. After about fifteen minutes, the rose-coloured precipitate begins to change into the green modification, the conversion being complete after some hours. The manganous sulphide is then separated by filtration, washed with dilute ammonium hydrogen sulphide solution, and dried in a current of hydrogen at 110°.

This change takes place also in absence of ammonium chloride, and for each concentration of the manganous salt there is a definite concentration of ammonia corresponding with the maximum velocity of the conversion. The latter is prevented by the presence of even a small proportion of hydroxylamine hydrochloride, and is retarded by ammonium chloride if this is added subsequently to the precipitation.

Green manganous sulphide is obtained either anhydrous or in a hydrated form, the content of water, which varies from 0 to 17% ($1H_2O$), being dependent on the concentration of the ammonia, the presence or absence of ammonium chloride, and the length of time during which the precipitate remains in contact with the mother liquor. Any hydrated green sulphide becomes anhydrous if left long enough in the liquid. This sulphide may be obtained crystalline if the solution is stirred during the formation of the precipitate, or if ammonia is first added to the solution of the manganous salt and ammonium hydrogen sulphide then gradually introduced. The crystals consist of black tetrakis-octahedra or icositetrahedra with green streaks, D 4·03, alabandite having D 3·92—4·06. Microphotographs of the crystals are reproduced.

Manganous sulphide may be precipitated from a faintly acid solution of a manganous salt by means of hydrogen sulphide if the passage of the gas is sufficiently protracted. The precipitate obtained in this way is red or orange-red, and, in dependence on the degree of acidity of the solution, is either anhydrous or hydrated to a maximum of 17% of water, corresponding with the

composition MnS,H_2O; under certain conditions, it is deposited in the form of doubly refracting crystals. Rose-coloured manganese sulphide, formed on precipitation of a solution of a manganous salt by means of the sulphide of an alkali metal, is amorphous. This, and also the red variety, are converted into the green modification by trituration.

In presence of a considerable proportion of sodium hydroxide, addition of sodium sulphide to a solution of a manganous salt gives, not the rose-coloured sulphide, but a white precipitate having the composition $MnS,3Mn(OH)_2$ or OH·Mn·O·Mn·S·Mn·O·Mn·OH.

T. H. P.

Salts of Complex Metallopyrophosphoric Acids. Arthur Rosenheim and Telemach Triantaphyllides (*Ber.*, 1915, **48**, 582—593).—It has long been known that the insoluble pyrophosphates of many metals dissolve in alkaline pyrophosphates to give solutions which fail to show many of the reactions of the metals. Some of the salts of the complex metallopyrophosphoric acids are described. They are comparable with Weinland and Ensgraber's salts of the ferriphosphoric acid (A., 1914, ii, 132).

Sodium manganipyrophosphate, $Na(MnP_2O_7),5H_2O$ (Christensen, A., 1884, 399), is obtained by dropping a solution of manganese sesquioxide in cold, concentrated hydrochloric acid into a saturated solution of sodium pyrophosphate. Potassium forms two *salts*, $K(MnP_2O_7),5H_2O$, pale violet, stable below 10°, and the *trihydrate*, which is pale red, and only decomposed by boiling water. The *ammonium* salt, $NH_4(MnP_2O_7),3H_2O$, is pale violet, and is hydrolysed by cold water. From it may be obtained the pink *silver* salt, $Ag(MnP_2O_7),3H_2O$, and the pink *barium* salt, $Ba(MnP_2O_7)_2,5H_2O$. They are all almost insoluble in cold water.

Salts of *chromipyrophosphoric acid* were prepared in a similar manner. Sodium forms a grey *octahydrate*, $Na(CrP_2O_7),8H_2O$, which passes into a pale green *pentahydrate* in a few days. Potassium gives the pale green *salt*, $K(CrP_2O_7),5H_2O$, and ammonium the *hexahydrate*, $NH_4(CrP_2O_7),6H_2O$, in grey, microscopic columns. In these salts, the complex anion is more sensitive towards hydrolytic agents than in the manganipyrophosphates.

Iron gives two sodium ferripyrophosphates, a reddish-grey powder, approximating to $Na_6Fe_2(P_2O_7)_3,9H_2O$, and a pale grey *compound*, $Na_8Fe_4(P_2O_7)_5,28H_2O$ (compare Pascal, A., 1908, ii, 193).

Sodium bismuthipyrophosphate, $Na(BiP_2O_7),3H_2O$, forms microscopic columns. *Sodium thallipyrophosphate*,

$$Na_5[Tl(P_2O_7)_2],6H_2O$$

or $Na(TlP_2O_7),Na_4P_2O_7,6H_2O$, crystallises in white needles.

Tripotassium molybdenum hexachloride (Chilessoti, A., 1903, ii, 730) was added to a solution of sodium pyrophosphate at 80—90°, when *sodium molybdenipyrophosphate*, $Na(MoP_2O_7),12H_2O$, separated as a precipitate of brown prisms. Solutions of tervalent uranium and titanium, however, were immediately oxidised, with evolution of hydrogen.

Vanadium ammonium alum gave with alkaline pyrophosphates a flocculent, green precipitate of *vanadium pyrophosphate*, $V_4(P_2O_7)_3,30H_2O$, which dissolved in excess to give grass-green solutions, from which, however, no complex salts could be crystallised.

Similarly, cobaltic sulphate gave a stable, deep green solution in excess of alkaline pyrophosphate, but no crystalline salt. However, the analogous sodium hexamminecobaltipyrophosphate, $Na\{[Co(NH_3)_6]P_2O_7\},11{\cdot}5H_2O$, is well known (Jörgensen).

Cerium pyrophosphate, $Ce_4(P_2O_7)_3,12H_2O$, also dissolves in excess of sodium pyrophosphate. The authors are able to confirm Carney and Campbell's discovery (A., 1914, ii, 583) that cerium and thorium can be quickly and quantitatively separated by reason of the solubility of cerium pyrophosphate in hydrochloric acid.

J. C. W.

Investigations at High Temperatures. VII. Iron and Carbon. Otto Ruff and Walter Bormann (*Zeitsch. anorg. Chem.*, 1914, **88**, 397—409. Compare A., 1911, ii, 897).—The measurements of Hanemann (A., 1914, ii, 56) and Wittorff (A., 1912, ii, 259) are criticised, and the accuracy of the previous solubility curve confirmed by new experiments. Iron saturated with 7·4% of carbon boils at 2650° under 36 mm. pressure, and the vapour contains 0·92% C. Pure iron boils at 2450±50° at the same pressure.

C. H. D.

Hypereutectic Alloys of Iron and Carbon. Otto Ruff (*Zeitsch. anorg. Chem.*, 1914, **89**, 39—47).—Polemical against Hanemann (A., 1914, ii, 56; compare A., 1911, ii, 897). Photomicrographs are given, with the remark that the constituent resembling ledeburite is not necessarily identical with the eutectic.

C. H. D.

Boron Steels. Gerhard Hannesen (*Zeitsch. anorg. Chem.*, 1914, **89**, 257—278).—The iron–boron system has been investigated, using alloys prepared by fusing Goldschmidt's ferro-boron with low-carbon steel, containing 0·07% of carbon. For analysis, the alloys are fused with sodium carbonate, extracting the borate with hot water, boiling with hydrochloric acid in a reflux apparatus to remove carbon dioxide, neutralising with potassium hydroxide and methyl-orange, and then titrating in the usual manner, using glycerol.

The fusions are carried out in hydrogen. When more than 4% of boron is present, ten minutes' heating at 1400—1500° leads to the formation of a grey powder, which does not contain oxide or nitride, but has not been further investigated. In each experiment, 20 grams of alloy have been used, and the series has been examined as far as 8·5% of boron. The freezing-point curve falls to a eutectic point at 1164° and 4% of boron, and then rises to a maximum at 1351°, corresponding with the compound Fe_5B_2. According to the thermal data, which are not very numerous, the

primary crystals from 0 to 1·38% B are solid solutions in δ-iron, and from 1·38 to 4% B solid solutions in γ-iron. The composition of the compound is confirmed by microscopical examination. The crystals of Fe_5B_2 are rhombic in section, and frequently elongated.

The temperature of transformation of γ- into β-iron is lowered by boron, as is that of β- into α-iron. Both β- and α-iron retain boron in solid solution. A constituent resembling pearlite is also observed, and a thermal arrest at 713° is present in alloys containing from 0·25 to 7·3% of boron, corresponding with the liberation of the compound Fe_5B_2 from solid solution. Rapidly cooled alloys give a martensitic structure. The alloys, including the pure boride, are ferromagnetic. The quenched alloys are softer than those which are slowly cooled. Those which contain primary Fe_5B_2 are much harder, the compound scratching corundum.

C. H. D.

Electroplating with Cobalt. Herbert T. Kalmus, C. H. Harper, and W. L. Savell (*J. Ind. Eng. Chem.*, 1915, **7**, 379—399).—Of several cobalt solutions which were found to be suitable for electro-plating with cobalt, the following yielded the best results: (1) crystallised cobalt ammonium sulphate, 200 grams per litre of water; (2) cobalt sulphate 312 grams, sodium chloride 19·6 grams, boric acid nearly to saturation, water 1000 c.c. From these solutions, cobalt plates on brass, iron, steel, copper, tin, German silver, lead, and Britannia metal, the coating being firm, adherent, hard, and uniform. When polished, the surface, although brilliantly white, has a slightly bluish tint. Compared with nickel plating, the plating with solution (1) is four times, and with solution (2) fifteen times, more rapid, but the voltage required is greater than that used for most nickel-plating baths. Since cobalt is harder than nickel, a much thinner coating of cobalt will offer the same protective coating as a greater weight of nickel deposit; thick deposits of cobalt are superior in appearance and character to those of nickel.

W. P. S.

Investigations at High Temperatures. VIII. Cobalt and Carbon. Otto Ruff and F. Keilig (*Zeitsch. anorg. Chem.*, 1914, **88**, 410—423. Compare A., 1912, ii, 1176).—The solubility of carbon in liquid cobalt increases from 2·4% at the eutectic point, 1300°, to 7·3% at 2415°, the boiling point of the solution under 30 mm. pressure. The curve has an inflexion corresponding approximately with the carbide, Co_3C. Pure cobalt boils at about 2415° under 30 mm. pressure. The saturated vapour contains 2·0% of carbon. The carbide decomposes so rapidly on cooling that it is absent even from quenched specimens.

C. H. D.

Ammonia Compounds of the Haloids of Divalent Cobalt. Wilhelm Biltz and Bruno Fetkenheuer (*Zeitsch. anorg. Chem.*, 1914, **89**, 97—133. Compare A., 1913, ii, 968).—The equilibria are more complex than in the corresponding nickel series, owing to the presence of solid solutions and polymorphic modifications,

whilst the investigations are also rendered difficult by the low melting points. The isobars are determined as in the previous paper, whilst the isotherms are determined in special flasks with vapour jackets, using an oil manometer in cases in which the vapour pressure is very small. The crystalline compounds prepared in the wet way are more suitable for experiment than the loose powders obtained in the dry way.

Hexa-amminocobaltochloride begins to decompose in ammonia gas at 130°; from 220° to 273° the diammine is stable. A saturated solid solution, violet in colour, exists between 152° and 175°, passing gradually into the hexa-ammine or diammine. Time is required for the formation of the solid solution, and in rapid heating this stage is not observed. The diammine melts at 273°. The isotherm at 137° also indicates the formation of the solid solution, and the absence of any intermediate compound. A mono-ammine is found between the diammine and the anhydrous salt, without any solid solution.

The heats of formation have been determined calorimetrically and tensimetrically, the former method giving the higher values, although the differences are less than for nickel.

The bromides cannot be investigated by the isobaric method, but the isothermal measurements indicate solid solutions between the hexa-ammine and the diammine. The latter melts at 260°. The mono-ammine does not form solid solutions.

Isotherms of the iodides have been determined at 137° and 181·5°. Partial miscibility in the solid state is found, but the hexa-ammine first passes into the diammine, which then enters into the solid solution, which is reddish-violet, the diammine being blue. The latter melts at 222°. A stable mono-ammine does not exist.

The pink diammino-chloride and bromide, and the blue iodide described above, are new, and are termed α-diammines. The β-chloride and bromide are blue, and the iodide green, and may be prepared from the hexa-ammines in a high vacuum over sulphuric acid. They have a higher vapour pressure than the α-modifications, and pass into the latter on heating. The reverse change has not been effected. On the ground of the colour differences, the α-compounds are considered to belong to the *cis*-series, and the β to the *trans*-series.

The methods of preparation are described. C. H. D.

The Ammonia Compounds of the Haloids of Divalent Nickel and Cobalt and their Relations to one Another. WILHELM BILTZ and BRUNO FETKENHEUER (*Zeitsch. anorg. Chem.*, 1914, **89**, 134—140. Compare preceding abstract).—Isothermal measurements clearly show the existence of a monoamminonickel chloride, differing little in vapour pressure from the diammine.

"Valency isobars" are drawn for each series of compounds, the ordinates being valency numbers and the abscissæ temperatures, an arbitrary pressure being taken. In this group of compounds, the affinity per molecule of ammonia increases in the hexa-

ammines in the order chloride–bromide–iodide, but in the monoammines the order is the reverse. C. H. D.

Investigations at High Temperatures. VI. Nickel and Carbon. Otto Ruff and Walter Bormann (*Zeitsch. anorg. Chem.*, 1914, **88**, 386—396. Compare A., 1912, ii, 354).—The freezing-point curve of nickel containing carbon in solid solution has been redetermined, and the eutectic point fixed at 1311° and 2·2% C. About 0·35% C is held in solid solution. The solubility of carbon in nickel increases with temperature up to 6·3% at 2075°, and remains constant to the boiling point 2490° under 30 mm. pressure. Pure nickel boils at 2340° under this pressure. Only 0·28% of carbon is present in the vapour at the boiling point. C. H. D.

Chemical Reactions at Low Pressures. Irving Langmuir (*J. Amer. Chem. Soc.*, 1915, **37**, 1139—1167).—An account is given of the author's studies of the reactions which occur when a gas is removed by a heated filament (compare A., 1913, ii, 209, 859; 1914, ii, 104, 412, 717; this vol., ii, 248).

Chlorine attacks tungsten at low pressures, with formation of the hexachloride, WCl_6. The velocity of the reaction reaches a maximum at about 1500° (abs. temp.), and becomes very small at higher temperatures.

When a carbon filament is heated in oxygen at very low pressures at about 1200° (abs. temp.), part of the oxygen reacts to form carbon dioxide, but another part forms an adsorption layer on the surface, which retards the velocity of the reaction, and probably consists of an extremely stable solid oxide of carbon. At higher temperatures, the rate of formation of this adsorption layer increases rapidly; when a certain quantity has accumulated, the compound begins to decompose, with production of carbon monoxide, the rate of this decomposition increasing as the temperature rises.

Since molybdenum evaporates much more readily than tungsten, it was expected that nitrogen would be removed more easily by a molybdenum than by a tungsten filament, but this was found not to be the case. It was found that the molybdenum lost weight at the same rate as in a vacuum, that the rate of removal was independent of the pressure, as in the case of tungsten, but that the amount of gas removed was only about one-tenth of that which would have been observed if every molybdenum atom combined with a nitrogen molecule. The reaction velocity has a strongly negative temperature-coefficient. In these experiments, a deposit of molybdenum collected on the bulb which had certain remarkable properties. When cooled by liquid air, it was capable of adsorbing large quantities of nitrogen, but not hydrogen. At the ordinary temperature, however, it slowly dissolved much hydrogen, which was given up slowly at 300°. Although the deposit contained a considerable amount of nitrogen, this gas could not be expelled at 360°; if heated in nitrogen at 250°, the gas was absorbed, and was not liberated on heating at

360° in a vacuum. The deposit reacted rapidly with water vapour at the ordinary temperature, with production of hydrogen. It is probable that the molybdenum is in an atomic state of division as a result of being deposited atom by atom by the decomposition of the unstable compound formed in the "unsuccessful collisions." Molybdenum deposited on the bulb in a high vacuum does not exhibit any of these characteristics.

Carbon monoxide in a bulb with a tungsten filament behaved exactly like nitrogen; each atom of tungsten combined with one mol. of carbon monoxide, probably with formation of a compound, WCO. The rate of attack is independent of the pressure, probably owing to the velocity of the reaction being so great that the rate of evaporation of the compound formed determines the rate of reaction. The temperature-coefficient of the reaction velocity was strongly negative.

A platinum filament at temperatures above 1600° (abs. temp.) gradually causes the removal of oxygen at low pressures. The oxygen combines with the platinum atoms as fast as they evaporate from the filament, and forms the compound PtO_2, which collects on the bulb as a brown deposit.

When a tungsten filament is heated at 3000° (abs. temp.) in a vacuum, a black deposit of tungsten is formed on the bulb. On admitting chlorine into the bulb at a low pressure, neither the deposit nor the filament is attacked, even if the bulb is heated at 200°. If, however, the filament is now heated at a high temperature while the bulb is kept cool, the deposit on the bulb soon disappears.

When a mixture of carbon monoxide and oxygen was admitted into a bulb containing a platinum filament, and the latter was heated, the rate of removal was found to be directly proportional to the pressure of the oxygen, but inversely proportional to that of the carbon monoxide. A similar reaction takes place when a mixture of hydrogen and oxygen is employed, the rate of reaction at low temperatures being directly proportional to the pressure of the oxygen, and inversely proportional to that of the hydrogen.

If a positive potential of about 100 volts is applied to an auxiliary electrode in a bulb containing a heated filament, electrons are given off from the filament, and in passing through the gas may produce ionisation. The positive ions are attracted to the hot filament, and strike it with great velocity. Under these conditions, reactions occur which would not take place otherwise. If the gas is nitrogen, the positive ions combine with the tungsten filament to form the nitride, WN_2, even at temperatures at which normally the tungsten does not appreciably volatilise. Similar effects have been observed with hydrogen and carbon monoxide.

E. G.

Iso- and Hetero-Poly-acids. X. Enneabasic Hetero-Poly-acids. Arthur Rosenheim and Hermann Schwer (*Zeitsch. anorg. Chem.*, 1914, **89**, 224—240. Compare A., 1913, i, 413; 1914, ii, 58).—The 12-borotungstates have been further investigated, in order to

determine their basicity. Sodium 12-borotungstate has the composition $Na_5H_4[B(W_2O_7)_6],27H_2O$, and is isomorphous with the similarly constituted sodium metatungstate,

$$Na_6H_4[H_2(W_2O_7)_6],27H_2O.$$

The conductivity corresponds with a neutral pentabasic salt, but the neutralisation curve shows that at least two more of the hydrogen atoms are replaceable. The *guanidinium* salt,

$$(CH_6N_3)_6H_3[B(W_2O_7)_6],$$

forms silvery scales, and the *silver* salt, $Ag_5H_4[B(W_2O_7)_6],7H_2O$, is a white, crystalline precipitate. Enneabasic salts have not been obtained with certainty.

Many salts have been prepared having the general formula $R'_3H_6[M'''(MoO_4)_6],7H_2O$, where R′ = potassium or ammonium, and M‴ = iron, chromium, or aluminium. Two *guanidinium* salts were obtained, $(CH_6N_3)_4H_5[Cr(MoO_4)_6],6H_2O$ being sparingly soluble, and $(CH_6N_3)_3H_6[Cr(MoO_4)_6],7H_2O$ more readily soluble. A *barium* salt, $Ba_2H_5[Cr(MoO_4)_6],5H_2O$, is also obtained. An attempt to resolve ammonium strychnine chromi- and alumino-molybdates into optical isomerides failed.

Alumino- and chromi-tungstates of definite composition have not been obtained, but the corresponding ferri-compounds are known. *Ammonium* and *potassium* salts of the composition

$$R'_4H_5[Fe(WO_4)_6],9H_2O$$

are described, as well as a *guanidinium* salt,

$$(CH_6N_3)_3H_6[Fe(WO_4)_6,5H_2O.$$

The salt obtained by Rogers and Smith (A., 1905, ii, 38) may be written $(NH_4)_4H_5[Mn(WO_4)_6],9H_2O$, thus falling into the above series, but the cerium salt described by Barbieri (A., 1911, ii, 291), $(NH_4)_3CeMo_7O_{24},12H_2O$, is a double salt of the paramolybdate series, although its reddish-yellow colour suggests that the tervalent cerium is partly in a complex form. C. H. D.

Hetero-poly-acids Containing Vanadic Acid. III. [Constitution of Tungstates.] Wilhelm Prandtl (*Ber.*, 1915, **48**, 692—698).—It has been shown that the complex vanadiselenites and molybdates are derivatives of a hexavanadic acid (A., 1912, ii, 167; 1913, ii, 61). In a fourth paper, the vanaditungstates will be discussed, but before doing this, the author finds it to be advisable to enquire into the constitution of the tungstates.

Three series of tungstates are generally recognised: (1) the so-called normal tungstates, $M_2'WO_4$, which are hydrolysed to hydrogen tungstates by water; (2) the paratungstates,

$$3M_2'O,7WO_3,nH_2O,$$

which are formed by the action of dilute acids on the hydrogen tungstates; (3) the metatungstates, $M_2'O,4WO_3,nH_2O$, which are formed by the continued action of hydrogen ions on the paratungstates.

The formation of the paratungstates is analogous to the formation of the paramolybdates, and therefore, like them, they are regarded as compounds of 1 mol. of the tritungstate with 4 mols. of the hydrogen tungstate. Their derivation from normal

tungstates is expressed thus: $M_2WO_4 + H_2O = MHWO_4 + MOH$ and $7MHWO_4 + H_2O = M_2H_4W_3O_{12}, 4MHWO_4 + MOH$. If, from analogy to the vanadates and molybdates, the action of hydrogen ions proceeds still further, hexatungstates should result, thus:

$$2M_2H_4W_3O_{12} = M_3HW_6O_{20} + MOH + 3H_2O,$$

and the so-called "metatungstates" are, indeed, the hexatungstates.

It is shown by many examples that the very obscure reactions of metatungstates can be explained most readily if the compounds are regarded as hexatungstates. Thus, Leontowitsch described a compound, $Na_2O,6WO_3,15H_2O$, which he obtained by the action of hydrochloric acid on sodium "metatungstate,"

$$Na_2O,4WO_3,10H_2O$$

(A., 1905, ii, 325). This reaction becomes explicable when both compounds are regarded as hexatungstates, thus:

$$Na_3HW_6O_{20},14H_2O + HCl = Na_2H_2W_6O_{20},14H_2O + NaCl.$$

It is not yet possible to determine the molecular weights of tungstates, but the formulæ of the vanadates, on which the above is based, were confirmed by such means (Prandtl and Hess, A., 1913, i, 815). J. C. W.

Action of Stannous Chloride on Sulphuric Acid and on Sulphurous Acid. Reginald Graham Durrant (T., 1915, **107**, 622—638).—When stannous chloride reacts with excess of concentrated sulphuric acid, hydrogen chloride is set free between 20° and 90°, and at a higher temperature (130—200°) sulphur dioxide is liberated, with the formation of stannic sulphate,

$$SnSO_4 + 2H_2SO_4 = Sn(SO_4)_2 + 2H_2O + SO_2.$$

When heated alone, stannic sulphate gives off sulphur dioxide between 360° and dull redness, $SnSO_4 = SnO_2 + SO_2$. The reaction between stannous chloride and dilute sulphuric acid is of complicated character. Hydrogen sulphide is liberated, but this appears to be formed from sulphur dioxide as an intermediate product. In no case is stannous chloride completely oxidised by dilute sulphuric acid, and no oxidation seems to occur unless the solutions are warmed.

Sulphur dioxide reacts with solutions of stannous chloride at the ordinary temperature, with the result that the stannous salt is partly or completely oxidised. The quantitative result depends on the relative quantities of the sulphur dioxide, stannous chloride, and hydrochloric acid, and also on the concentration. The primary reaction is $3SnCl_2 + 6HCl + H_2SO_3 = 3SnCl_4 + 3H_2O + H_2S$, and this is accompanied by the reactions $2H_2S + H_2SO_3 = 3H_2O + 3S$, $2H_2S + SnCl_4 = SnS_2 + 4HCl$, $H_2S + SnCl_2 = SnS + 2HCl$. The reverse reaction, $SnCl_4 + H_2SO_3 + H_2O = SnCl_2 + 2HCl + H_2SO_4$, also occurs to a small extent.

For complete oxidation, the quantities of stannous chloride, sulphur dioxide, and hydrochloric acid must be approximately in the ratio 3 : 1·55 : 6.

In presence of excess of hydrochloric acid, the speed of the

reaction changes approximately in accordance with the equation for a bimolecular reaction. H. M. D.

A New Tin-Sulphur Compound, Sn_2S? GOTTLIEB EPPRECHT (*Chem. Zeit.*, 1915, **39**, 341—342).—A mass of grey crystals was found at the bottom of a furnace used for the recovery of tin from solutions employed in the treatment of silk. The crystals had D 5·77, and consisted of tin 84·1%, sulphur 13·6%, iron 2·0%, and other substances 0·3%, and, apparently, consisted of a mixture of Sn_2S 95·4%, FeS_2 4·3%, and other substances 0·3%. W. P. S.

Physico-chemical Studies on Antimony. ERNST COHEN and J. C. VAN DEN BOSCH (*Zeitsch. physikal. Chem.*, 1915, **89**, 757—760).—Density determinations of antimony which has been chilled by pouring the molten metal into a paper cylinder surrounded by solid carbon dioxide and alcohol yield the mean value D_4^{25} 6·6899. When this material, finely powdered, is heated at 102·5° for some hours, the density becomes D_4^{25} 6·6786. From these results, the conclusion is drawn that the chilled metal is made up of a modification of antimony, which is changed into a second variety at 102° with a measurable velocity of change. This result is confirmed by dilatometric measurements, which place the temperature of transformation very near 101°. J. F. S.

Allotropy of Bismuth. II. ERNST COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1236—1238).—Earlier observations seemed to show the existence of a transition temperature at 75° (compare A., 1913, ii, 779). It is now found that this temperature varies with the previous history of the bismuth. Finely divided bismuth, which had been in contact with a 10% solution of potassium chloride for twelve hours, was found to diminish in volume at 70°, although the same sample of metal, before treatment with the salt solution, showed no change in volume at this temperature. In the previous experiments, the volume increased at temperatures between 75° and 100°, whereas the new experiments with bismuth, treated with a salt solution, show a decrease in volume at these temperatures. H. M. D.

Bismuth Suboxide. F. TREUBERT and L. VANINO (*Zeitsch. anal. Chem.*, 1915, **54**, 255—258. Compare this vol., ii, 170, 267).—Further evidence is given of the non-existence of bismuth suboxide. The substance, as prepared by different investigators, has had a composition equivalent to that of BiO, but the specific gravities of the specimens have varied from 7·17 to 8·55. When bismuth salts are reduced by alkaline stannous chloride, the precipitate consists of a mixture of metallic bismuth and bismuth hydroxide, or of metallic bismuth alone, according to the degree of reduction. W. P. S.

Reduction of Iron Oxides by Platinum. Magnetic Susceptibility of Iron-bearing Platinum. R. B. SOSMAN and J. C. HOSTETTER (*J. Washington Acad. Sci.*, 1915, **5**, 293—303).—It has been found that platinum crucibles increase in weight when

employed for heating the oxides of iron at high temperatures. The investigation of this effect has shown that platinum acts on both ferric oxide and magnetite at 1200° under low oxygen pressures. Oxygen is evolved, and a solid solution of iron in platinum is formed. At 1600°, this change takes place under the oxygen pressure of the atmosphere. This pressure is, however, sufficient to prevent the change from taking place at 1200°, and since this temperature is seldom exceeded in the ignition of ferric oxide in analytical work, it follows that this is not appreciably reduced by heating in contact with platinum in the open air.

From some observations on the magnetic susceptibility of iron-platinum alloys, it is found that the susceptibility is not in any way proportional to the iron content. The magnetic properties cannot therefore be made use of in estimating the quantity of iron in platinum. H. M. D.

Solubility of Palladium in Selenic Acid; Palladous Selenate. KARL HRADECKY (*Monatsh.*, 1915, **36**, 289—297).—It is shown that palladium, like gold and silver, dissolves completely in selenic acid. Solution occurs at ordinary temperature when the metal is in the spongy condition or when it is finely divided if a 67% acid is used. When the coherent metal in the form of foil or wire is used, solution only occurs very slowly, even on heating. A deep, reddish-brown solution is produced, which on concentrating gives a mixture of palladous selenate and selenious acid. The pure compound, palladous selenate ($PdSeO_4$), is obtained by dissolving palladium in a mixture of selenic acid and nitric acid. It forms small, dark brownish-red, hygroscopic, rhombic prisms. When warmed with hydrochloric acid (conc.), chlorine is evolved. It forms double salts with ammonium sulphate and ammonium selenate when a mixture of the two salts is crystallised from a solution in concentrated hydrochloric acid. Palladous selenate softens at a red heat and then decomposes; D. 6·5. It is shown also that alloys of gold and silver, and gold, silver, and palladium, dissolve in selenic acid. The possible use of selenic acid in the analysis of such alloys is considered. Platinum-silver alloys are decomposed by selenic acid, the silver passing into solution, whilst the platinum remains undissolved. J. F. S.

Mineralogical Chemistry.

Variation in Composition of Natural Gas from Different Sands in the same Field. G. A. BURRELL and G. G. OBERFELL (*J. Ind. Eng. Chem.*, 1915, **7**, 419).—The following results

were obtained on the analysis of two gases from different sands in a gas field near Trafford City, Pa., U.S.A.:

	Murraysville Sand.	Elizabeth Sand.
Depth of sand	1700 ft.	2295 ft.
Rock pressure	190 lb. per sq. in.	1000 lb. per sq. in.
Composition of gas:		
Carbon dioxide	trace	trace
Methane	98·8 per cent.	94·0 per cent.
Ethane	none	5·2 ,,
Nitrogen	1·2 per cent.	0·8 ,,

Other similar gases showed the same variation in composition; the gas from the shallower sand invariably contained less of the higher paraffin hydrocarbons than did that from the deeper sand. W. P. S.

Origin of Petroleum. N. Kishner (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1428—1441).—Wide acceptation has been accorded in recent years to the hypothesis of the vital origin of petroleum, mainly in consequence of the optical activity of the latter, but the author shows the possibility of the formation of hydrocarbons, such as are found in petroleum, by purely inorganic processes. The principal points discussed are briefly as follows. The combination of hydrogen with carbon at high temperatures; the presence in meteorites of iron, etc., carbon, gases, including hydrogen, hydrocarbons, including methane and even solid hydrocarbons in the form of ozokerite, and the presence of hydrocarbons in the atmosphere of red stars; the consequent possibility of hydrocarbons being formed during the early stages of the earth's history, when the conditions were such as to render vital phenomena impossible; the eruption of hydrocarbons from volcanoes; the liberation, and escape to regions of lower pressure, of hydrocarbons formed in the depths of the earth from hydrogen and carbon dissolved in liquid metal, in which the hydrocarbons would be less soluble; the condensation, without carbonisation, of the comparatively simple hydrocarbons thus formed into more complex forms under the influence of high temperatures and pressures exerted over long periods of time (compare Ipatiev's recent work); the possibility of optical activity resulting from bacterial action or from the differential effect of the earth's magnetism, extending over geological periods of time, on the chemical transformations undergone by optical antipodes. T. H. P.

The Quantitative Chemical Composition of the Stassfurt Salt Deposits. M. Rózsa (*Zeitsch. anorg. Chem*, 1914, **90**, 377—385. Compare this vol., ii, 355, 356).—The high ratio of anhydrite to rock salt in the deposits, in comparison with that which would be expected from the composition of sea water, is accounted for by the shrinking of large areas of sea, followed by successive washings with concentrated solutions in consequence of earth movements. The periodicity of the layers is attributed to climatic influences. C. H. D.

Bornite as Silver Precipitant. CHASE PALMER (*J. Washington Acad. Sci.*, 1915, **5**, 351—354).—The constitution of bornite, a sulphide of iron and copper which is frequently associated with native silver, has been examined by the investigation of its action on solutions of silver sulphate. Fragments of the mineral, which appeared to be free from chalcopyrite and chalcocite, were found to correspond fairly well with the formula Cu_5FeS_4.

The finely ground mineral was heated on a water-bath for several hours with a solution of silver sulphate, and the solution and solid residue were examined. The analytical data show that for each atom of copper which dissolves, one atom of silver is present in the metallic condition and one atom in combination with sulphur. The reaction may therefore be represented by the equation $2Cu_5FeS_4 + 10Ag_2SO_4 = 10Ag + 5Ag_2S,Fe_2S_3 + 10CuSO_4$. The results indicate that the copper present in bornite is cuprous, and the mineral may accordingly be represented by the formula $5Cu_2S,Fe_2S_3$. H. M. D.

Lublinite, the Monoclinic Modification of Calcium Carbonate. RICHARD LANG (*Centr. Min.*, 1915, 298—305. Compare A., 1914, ii, 665).—A reply to Mügge (this vol., ii, 358). L. J. S.

Presence of Monazite in the Sands and Arenaceous Formations of Southern Somaliland. ETTORE ARTINI (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 555—558).—The author has previously observed the presence of monazite in the sand of the Arabian Desert and in the arenaceous formation known as Nubian Sandstone, the latter being regarded as the source of the monazite in the former. The same mineral has now been found in the sand of Giuba, Southern Somaliland, this being regarded as derived from the arenaceous formations of the interior, which also contain monazite. T. H. P.

Labradorite from Kamenoi Brod, Russia. O. GROSSPIETSCH (*Tsch. Min. Mitt.*, 1914, **33**, 27—47).—The material consists of a dark grey crystal aggregate displaying a blue sheen. The dark colour is due to numerous minute acicular enclosures arranged parallel to the vertical crystallographic axis. D 2·6982. Analysis by R. Görgey gave the following results; allowing for enclosed impurities, these results give the formula

$$Ab_{39\cdot5}An_{56\cdot3}Or_{4\cdot2}.$$

The refractive indices are $\alpha = 1{\cdot}5561$, $\beta = 1{\cdot}5589$, $\gamma = 1{\cdot}5637$, and the extinction angles $-6°53'$ on (001) and $-20°55'$ on (010).

SiO_2.	Al_2O_3.	Fe_2O_3.	TiO_2.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
53·85	29·24	0·33	0·24	11·37	0·17	4·41	0·71	0·25	100·57

A summary and discussion are given of previously published analyses and optical determinations of labradorite, including those of M Schuster (1881) made on material from this same locality. L. J. S.

Chemical Composition of an Amphibolic Epidote from the Urals. S. Piña de Rubies (*Anal. Fis. Quim.*, 1915, **13**, 179—180).—This complex mineral is found on the summit of Mount Semitchelowietchny, and its probable origin is discussed. Analysis gave:

Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Na_2O.	K_2O.	SiO_2.	TiO_2.	H_2O.	Total.
17·96	7·67	2·74	18·97	4·93	0·71	0·04	45·64	0·59	1·89	101·14

and traces of MnO, P_2O_5, CO_2. A. J. W.

Some Remarkable Metamorphic Phenomena of Contact of the Granite in Madagascar. A. Lacroix (*Compt. rend.*, 1915, **160**, 724—729).—A detailed account of the examination on the spot and in the laboratory of a metamorphosed, azoic, sedimentary formation in the High Plateau of Madagascar, consisting of alternations of quartzites, limestones, and schists, metamorphosed by granite and also by a large number of pegmatitic veins. The marbles, instead of containing the white diopside, tremolite, or actinolite usual in this district, contain an abundance, in certain beds, of a new type of amphibole, which the author has named *imerinite*; it has the composition:

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.
53·73	0·41	2·72	4·72	4·70	20·60

CaO.	Na_2O.	K_2O.	F.	H_2O.
2·73	7·42	1·82	0·92	0·85

Cubes of pyrites are locally abundant, together with some galena. A microscopic examination shows that the limestones are still more complex, the presence of monazite being detected by this method. This monazite, on analysis, was found to be particularly poor in thoria (ThO_2=1·05%).

Further to the west there is another bed of granite, traversed by a pegmatite, containing two cerium minerals, namely, tscheffkinite, a silicotitanate, found on this occasion for the first time in nature in the form of well-defined crystals, and bastnæsite, a fluorocarbonate. The emanations from this granitic magma were rich in iron and titanium, which only appear to have penetrated slightly into the sediments, and to be mainly concentrated in the crevices. W. G.

Meteoric Iron from Premier Downs, Western Australia. E. S. Simpson and H. Bowley (*Bull. Geol. Survey, Western Australia*, 1914, **59**, 205—209).—Premier Downs I (analysis I by Simpson), weighing 112 grams, was found in 1911 at Premier Downs, on the Nullarbor Plains (E. S. Simpson, *op. cit.*, 1912, **48**). A second small mass, Premier Downs II, weighing 116 grams, is now described (anal. II by Bowley). It was found in the same district about eight miles from the first find, and, being very similar in appearance and structure, it no doubt belongs to the same meteoritic fall. The structure is octahedral. Kamacite forms 85% of the mass; tænite, graphite, and cohenite are conspicuous

Corresponding with the amount of combined carbon shown in the analysis, the percentage of cohenite would be 21·4, but this is largely in excess of the amount seen on cut surfaces; the material analysed, being from a saw-cut, probably contained an unduly large proportion of the brittle constituent of the mass.

	Fe.	Ni.	Co.	Cu.	C.	P.	S.	Si.	Mg.	Total.
I.	91·68	7·46	0·64	trace	0·04*	0·21	0·04	0·01	trace	100·08
II.	88·51	7·58	0·89	0·13	2·47†	0·31	nil	nil	nil	99·89

* Combined carbon. † Combined carbon, 1·41 ; graphite, 1·06.

L. J. S.

Meteoric Iron from Mount Edith, Western Australia. E. S. SIMPSON (*Bull. Geol. Survey, Western Australia*, 1914, **59**, 210—212. Compare A., 1914, ii, 481).—This mass measures $26 \times 21 \times 8$ inches, and was found in 1913. The structure is octahedral of medium coarseness; patches of eutectic are present in addition to the kamacite, tænite, and plessite. Analysis gave:

Fe.	Ni.	Co.	P.	Total.
89·45	9·45	0·75	0·35	100·00

L. J. S.

The Fisher (Polk Co., Minnesota) Meteorite. GEORGE P. MERRILL (*Proc. U.S. Nat. Mus.*, 1915, **48**, 503—506).—The several stones (total weight preserved, 9900 grams) fell on April 9th, 1894. They show primary, secondary, and tertiary crusts, and belong to Brezina's group of intermediate chondrites. Under the microscope is seen a confused aggregate of irregular granules of olivine and pyroxene interspersed with numerous imperfectly outlined chondrules, consisting of olivine or pyroxene with some maskelynite; small patches of nickel-iron and iron sulphide are also present. Analysis by J. E. Whitfield of the metallic portion (11·44%) gave I, and of the silicate portion (88·56%) II. The bulk composition of the stone is given under III. D 3·37.

	Fe.	Ni.	Co.	SiO_2.	Al_2O_3.	FeO.	MnO.	NiO.	CaO.	MgO.	Chromite.	Total.
I.	85·00	14·15	0·74	—	—	—	—	—	—	—	—	99·89
II.	—	—	—	43·70	4·96	18·27	0·38	0·23	2·17	29·38	0·80	99·91
III.	9·72	1·62	0·08	38·70	4·39	16·18	0·34	0·20	1·94	26·02	0·71	99·90

Traces of sulphur, sodium, and copper are present, but no barium, strontium, zirconium, or potassium. L. J. S.

Meteoric Stone of Appley Bridge (Wigan, Lancashire). W. C. JENKINS and E. L. RHEAD (*Monthly Notices R. Astron. Soc.*, 1914, **75**, 92—96).—This stone, weighing about 33lb., fell on October 13th, 1914. It consists of olivine (63·43%), enstatite (31·5), and troilite (5·06), with a small amount of metallic iron. D 3·336. Analysis gave:

SiO_2.	Fe.	Ni.	O.	MgO.	CaO.
39·7	20·72	1·3	5·25	23·64	trace

P.	S.	Al_2O_3.	Na_2O,K_2O,Cl.	Total.
0·23	1·84	6·2	[1·12]	100·00

L. J. S.

Analytical Chemistry.

Paraffined Apparatus for Volumetric Analysis. G. POVARNIN (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1898—1905).—In order to avoid certain of the inconveniences encountered in volumetric analysis, the author recommends that the measuring vessels, bottles for stock solutions, etc., be coated internally with a thin layer of paraffin wax. Perfectly white, crystalline paraffin wax, m. p. 55°, should be employed, and, before use, should be freed from any mechanical admixtures by fusion and decantation, or by filtration through a hot filter. The use of solutions of the wax in commercial amyl acetate, ether, or chloroform does not give good results. Methods for coating pipettes, burettes, bottles, etc., are described.

The ordinary dilute solutions employed in volumetric analysis are without action on the wax, and wet it very slightly indeed; this slight wetting seems to be conditioned by the inclusion of water by minute crystals of the paraffin wax, and it is possible that such crystallisation would be retarded by mixing ceresin with the wax. The general advantages of paraffined apparatus are that the necessity of keeping the interior of measuring vessels free from fatty matter is avoided, and that water vapour from standard solutions does not condense on the upper parts of the vessels. Paraffined pipettes deliver completely and rapidly, and, in general, need not be washed out during use; they should, however, be re-calibrated. Solutions of alkali hydroxide do not change in titre when stored in paraffined bottles, contact of the solutions with the glass being avoided. With iodine solutions or alcoholic alkali solutions, paraffined vessels cannot be employed. With burettes which are cleaned out each day or left filled with water overnight, the coating should extend over the whole inner surface; otherwise only the graduated part and the top need be waxed. The filling is best effected from the bottom of the burette, since with the ordinary constant-level burettes filled from the top, air-bubbles remain attached to the walls; this difficulty is, however, avoided by bending the delivery tube so as to deliver the liquid against the side of the burette and by filling the latter slowly. The correction for the volume occupied by the wax coating is about 0·0033 c.c. per 1 c.c., and this must be applied when absolute measurements are required. The height of the liquid, which is read at once, without waiting for the solution to drain from the walls of the burette, is determined, not by means of the meniscus, but at the line of contact of the liquid with the wax; an accuracy of 0·01 c.c. is easily attainable, but, owing to the slight wetting of the coating, this is diminished to about 0·02 c.c. Burettes with a white line at the back are unnecessary, and, indeed, do not give such sharp readings when waxed. The magnitude of a drop is rendered far more constant by the layer of wax. It is advan-

tageous to coat the upper two-thirds of the inner surface of the Erlenmeyer flasks used for titration. Measuring cylinders, when treated in this way, deliver their contents quantitatively, this being of special importance with small cylinders. Measuring flasks should be coated over a space on each side of the mark, or, if they are to be used as pipettes, over the whole of the inner surface.

Owing to the increased ease and speed with which waxed burettes and pipettes are manipulated, their use is of particular advantage in technical laboratories where large numbers of analyses are carried out. T. H. P.

Use of the Interferometer for the Analysis of Solutions. LEASON H. ADAMS (*J. Amer. Chem. Soc.*, 1915, **37**, 1181—1194).—A description is given of the Zeiss interferometer, and suggestions are made with reference to its applicability to chemical analysis. The instrument enables the single varying constituent in a solution to be estimated with ease, rapidity, and accuracy. As an example, it is stated that a mixture of potassium and sodium sulphates can be analysed by this means with an accuracy equal to, or even greater than, that of the most careful gravimetric methods. The only important source of error arises from differences in optical dispersion, and methods are described by means of which this can be obviated. E. G.

The Estimation of Minute Amounts of Acid and Basic Substances in Fluids of Vegetable or Animal Origin. A. STUTZER and W. HAUPT (*Biochem. Zeitsch.*, 1915, **69**, 305—308).—For estimation of acids or alkalis, a fluid can be distilled with 25 c.c. $N/5$-sodium hydroxide and 1 gram ammonium chloride, and the ammonia which distils over can be estimated by titration, and the amount compared with that obtained when distilled water is distilled with the same quantities of alkali and ammonia. Free acids can also be estimated by mixing the fluids with potassium iodide and iodate, and determining the iodine set free by titration in the presence of starch with $N/100$-thiosulphate solution. S. B. S.

Estimation of Chlorine, Bromine, and Iodine in the Presence of Each Other. JULIUS BEKK (*Chem. Zeit.*, 1915, **39**, 405—406).—A modification of Baubigny's method (compare A., 1911, ii, 532) is recommended. The three halogens are precipitated together as their silver salts, collected, dried, and weighed. The mixed salts are then heated for two hours at 95° with 2 grams of potassium dichromate and 30 c.c. of concentrated sulphuric acid (these quantities are sufficient for 0·4 gram of silver salt); the iodine is thus converted into iodic acid, whilst the chlorine and bromine are expelled. After the last traces of chlorine and bromine have been removed by a current of air, the mixture is cooled, diluted to 400 c.c., filtered, and the iodic acid reduced by the gradual addi-

tion of concentrated sodium sulphite solution; a large excess of the latter must be avoided. The silver iodide is collected, dried, and weighed; its quantity gives the amount of iodine present. The filtrate from the silver iodide contains the silver which was combined with the chlorine and bromine; it is precipitated by the addition of potassium iodide, the silver iodide is collected, and weighed. The amounts of chlorine, bromine, and iodine present originally are then calculated from the three weights obtained.

W. P. S.

Method for the Titration of Small Amounts of Haloids. FRANKLIN C. MCLEAN and DONALD D. VAN SLYKE (*J. Amer. Chem. Soc.*, 1915, **37**, 1128—1134).—A method for estimating small quantities of haloids is described which is based on Bang's method (A., 1913, ii, 446).

The haloid is precipitated in presence of a known amount of nitric acid, preferably about 1 gram, with excess of 0·04*N*- or 0·02*N*-silver nitrate. After the precipitate has been coagulated by shaking with one or two drops of octyl alcohol, the mixture is filtered. In the case of iodides, filtration is not necessary. The excess of silver is then estimated by titration with 0·02*N*- or 0·01*N*-potassium iodide which has been standardised against the silver nitrate solution. Just before titrating, 4 grams of the following solution are added for each gram of nitric acid present: trisodium citrate, $Na_3C_6H_5O_7,5\frac{1}{2}H_2O$, 446 grams; sodium nitrite, 19 grams; soluble starch, 2·5 grams; water to make the total volume 1000 c.c. The nitrite serves to liberate iodine; the citrate regulates the acidity of the solution, whilst the starch is for the end reaction. By means of this method, quantities of haloid as small as 0·5 mg. mol. can be estimated with an accuracy of 0·1%.

E. G.

Estimation of Chlorides in Cheese. ELFREIDA C. V. CORNISH and JOHN GOLDING (*Analyst*, 1915, **40**, 197—202).—The cheese is heated in a flask with concentrated sulphuric acid, and the liberated hydrochloric acid collected in an absorption vessel containing *N*/10-silver nitrate solution to which has been added 50% of its volume of nitric acid. A tube is fitted into the neck of the flask and passes into the absorption vessel, a current of air being drawn through the apparatus during the heating process. The excess of silver nitrate is titrated in the usual way with thiocyanate solution.

W. P. S.

Estimation of Oxygen in Water. JAN SMIT (*Chem. Weekblad*, 1915, **12**, 476—481).—A criticism of the method recommended in the Dutch *Codex Alimentarius* for the estimation of oxygen in water. The author has obtained better results with a solution of sodium hydroxide and potassium iodide of twice the strength.

A. J. W.

Absorption of Chlorine by Water as an Index of Quality. I. A. ZALESKI and N. A. ELMANOVITSCH (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1270—1283).—The absorptive capacity of water for

chlorine is determined by addition of an exact volume of clear bleaching powder solution to a definite volume of the water (usually 4 litres), followed, after a certain time, by estimation of the free chlorine present by titration with $N/50$-thiosulphate solution; the result is expressed in mg. of chlorine absorbed per litre of the water. Any marked increase in the chlorine absorption indicates contamination of the water with the products of protein decomposition. For the water of the Neva, the mean value is 7·5—8, its oxygen absorption, similarly expressed, being 18—20.

T. H. P.

Oxidation of Sulphides with Potassium Iodate. REGINALD S. DEAN (*J. Amer. Chem. Soc.*, 1915, **37**, 1134—1137).—Andrews (A., 1903, ii, 686) has shown that if potassium iodate is added to a solution of iodine in a liquid containing at least 50% by volume of concentrated hydrochloric acid, the iodine is gradually converted into iodine monochloride, and the end of the reaction may be ascertained by using chloroform as the indicator. This method has now been applied to the estimation of sulphides.

It has been found that the quantity of iodate solution required for the oxidation of the sulphides of cadmium, zinc, and lead corresponds with that demanded by the equation

$$3MS + 3KIO_3 + 12HCl = 3MCl_2 + 2S + H_2SO_4 + 3KCl + 3ICl + 5H_2O.$$

When a smaller proportion of hydrochloric acid is present, however, the amount of iodate is more nearly that required by the equation $2MS + KIO_3 + 6HCl = 2MCl_2 + 2S + KCl + ICl + 3H_2O$. In the case of antimony sulphide, the oxidation at low concentrations takes place thus:

$$2Sb_2S_3 + 5KIO_3 + 30HCl = 4SbCl_5 + 6S + 5KCl + 5ICl + 15H_2O,$$

whilst with increasing concentration it gradually attains the maximum, as shown by the equation

$$Sb_2S_3 + 4KIO_3 + 18HCl = 2SbCl_5 + 2S + H_2SO_4 + 4ICl + 4KCl + 8H_2O.$$

In the case of arsenious sulphide, it was expected that oxidation would take place thus:

$$As_2S_3 + 3KIO_3 + 12HCl = 2AsCl_3 + 2S + H_2SO_4 + 3ICl + 3KCl + 5H_2O,$$

but the results showed only two-thirds of the iodate demanded by this equation.

E. G.

Estimation of Sulphide and Sulphate Sulphur, and the Action of Solvents on Vulcanised Rubber. HENRY P. STEVENS (*Analyst*, 1915, **40**, 275—281).—Sulphide sulphur in vulcanised caoutchouc may be estimated by treating the sample with a mixture of hydrochloric acid and ether in an atmosphere of carbon dioxide; the liberated hydrogen sulphide is absorbed in a vessel containing lead acetate solution, and the resulting lead sulphide is then estimated iodometrically. The caoutchouc swells gradually in the ether-acid mixture, and the hydrogen sulphide is finally expelled by boiling the mixture. The sulphate remains in the acid solution; this is separated, the caoutchouc residue is extracted repeatedly with hydrochloric acid, and the sulphate estimated in the extracts. The

reaction between litharge and sulphur does not proceed according to the equation $4PbO + 2S_2 = 3PbS + PbSO_4$; usually, the amount of sulphate sulphur does not exceed one-fourth of that of the sulphide sulphur. The following results were obtained on the analysis of three vulcanised litharge mixings: free sulphur, 0·04 to 1·21%; sulphide sulphur, 0·69 to 1·86%; sulphate sulphur, 0·10 to 0·34%; combined sulphur, 0·67 to 2·33%. The sums of these amounts agreed with the quantities of sulphur added, respectively. At the ordinary temperature, vulcanised caoutchouc dissolves gradually in a mixture of ether and hydrochloric acid, and the dissolved substance contains about 1·5% of sulphur; it also dissolves in a mixture of benzene and hydrochloric acid, and as the extracts obtained after the first one contain practically the same amount of sulphur, it may be assumed that vulcanised caoutchouc is homogeneous. Chlorohydrocarbons act similarly to a mixture of solvents and hydrochloric acid. W. P. S.

Volumetric Estimation of Polythionic Acids by Potassium Iodate. GEORGE S. JAMIESON (*Amer. J. Sci.*, 1915, **39**, 639—642).—A process described previously (A., 1914, ii, 777) for the estimation of sulphurous acid may be applied to the titration of thiosulphates and tetrathionates. With thiosulphates, the reaction proceeds according to the equation

$$Na_2S_2O_3,5H_2O + 2KIO_3 + 2HCl = Na_2SO_4 + K_2SO_4 + 2ICl + 6H_2O,$$

and in the case of tetrathionates,

$$2Na_2S_2O_6 + 7KIO_3 + 10HCl = 4H_2SO_4 + 2Na_2SO_4 + 2K_2SO_4 + 7ICl + 3KCl.$$

Dithionates, owing to their stability, cannot be estimated by this method, and their presence does not interfere with the titration of thiosulphates. W. P. S.

Gravimetric Estimation of Selenium. A. GUTBIER and F. ENGEROFF (*Zeitsch. anal. Chem.*, 1915, **54**, 193—205. Compare A., 1904, ii, 775; 1914, ii, 288).—Selenium dioxide is reduced quantitatively to selenium by hydrazine sulphate or hydrazine hydrate in dilute nitric acid solution; the hydrazine solution should be added to the cold selenium dioxide solution, and the mixture then heated in order to prevent the spray formed by the escaping nitrogen carrying off a certain amount of finely-divided selenium. The nitric acid solution of the selenium dioxide may be evaporated to dryness without loss of selenium, but a small loss occurs when the residue is heated for one hour. W. P. S.

Estimation of Selenium in Organic Compounds. HUGO BAUER (*Ber.*, 1915, **48**, 507—508).—The author has examined the methods of Frerichs (A., 1903, ii, 327), Becker and Meyer (A., 1904, i, 698), and Michaelis (A., 1898, i, 136), and finds that a modification of the last-named is the most trustworthy. The substance is heated with fuming nitric acid (1·5 c.c.) for five hours or so at 250°, and then the contents of the tube are transferred to a flask with a little water, and boiled under reflux with at least 100 c.c. of concentrated hydrochloric acid until the nitrous

fumes have disappeared. Elemental selenium is then precipitated by sodium sulphite, and weighed in a Gooch crucible.

A. MICHAELIS (*Ber.*, 1915, **48**, 873—874) endorses the method. J. C. W.

The Analysis of Nitrous Oxide for Physiological Work. WALTER M. BOOTHBY and IRENE SANDIFORD (*Amer. J. Physiol.*, 1915, **37**, 371—377).—Certain modifications in the Haldane apparatus are recommended which make the analysis more accurate. W. D. H.

Estimation of Nitrogen by Kjeldahl's Method. OTTO NOLTE (*Zeitsch. anal. Chem.*, 1915, **54**, 259—262).—Whilst the addition of sugar to the acid digestion mixture is necessary in the estimation of nitrogen in diphenylamine, methylindole, and tetramethylammonium bromide, the addition is of no advantage in the case of aniline sulphate, betaine hydrochloride, potassium ferrocyanide, hippuric acid, pyrrole, thiocarbimides, silver thiocyanate, and trimethylamine hydrochloride. Its use in the estimation of nitrogen in acetanilide, antipyrine, uric acid, caffeine, and silver cyanide tends to cause loss of nitrogen. W. P. S.

A Precipitant for Ammonia. (A Substitute for Nessler's Reagent.) SARA STOWELL GRAVES (*J. Amer. Chem. Soc.*, 1915, **37**, 1171—1181).—In view of the instability of Nessler's reagent and its tendency to produce a cloudiness in dilute solutions, the author has devised a reagent to serve as a substitute.

The reagent is prepared by adding 130 c.c. of water and 100 c.c. of cold, saturated solution of mercuric chloride to 80 grams of sodium chloride. The mixture is shaken until the sodium chloride has dissolved, and 70 c.c. of a saturated solution of lithium carbonate (1%) is added slowly, with shaking, so that mercuric oxide is not deposited on the sides of the flask. The solution is usually cloudy, owing to the presence of ammonia in the substances used, but if well shaken with 3—5 grams of talcum powder and filtered, a clear liquid can be obtained. The solution can be kept almost indefinitely in carefully stoppered bottles. The reagent is standardised against a solution of ammonium sulphate containing potassium sulphate. Estimations of ammonia are made by comparing with the nephelometer the cloudiness produced in the solution under examination with that produced in a standard ammonium sulphate solution. Before applying the reagent, a soluble starch solution is added to the liquid, in order that the precipitate may be kept in suspension long enough for nephelometric readings to be made.

The reagent, whilst being more stable than Nessler's reagent in presence of salts, is quite as sensitive. It precipitates ammonia quantitatively, and yields accurate results with the nephelometer. It can be applied directly in Kjeldahl estimations, thus obviating the necessity for distillation, and it is suggested that it may prove useful in water analysis. E. G.

Estimation of Non-Protein Nitrogen in Blood. ISIDOR GREENWALD (*J. Biol. Chem.*, 1915, **21**, 61—68).—Methyl alcohol as a precipitant for protein in blood is undesirable, for the reason (amongst others) that amino-acids added to the blood cannot be recovered quantitatively in the filtrate. Moreover, the extract contains about 0·003% of lipoid nitrogen. Although this is non-protein, it scarcely belongs to the same fraction as urea and amino-acids. If a 2·5% solution of trichloroacetic acid is substituted for methyl alcohol, the lipoids are precipitated with the proteins, and added amino-acids are recovered quantitatively in the filtrate. The filtrate may contain a trace of protein, which can be removed by shaking with kaolin. The normal amount of non-protein nitrogen is 30 mg. per 100 c.c. of human blood. W. D. H.

Estimation of Phosphorus Hydride. H. RECKLEBEN (*Zeitsch. anal. Chem.*, 1915, **54**, 241—252).—In the estimation of phosphorus hydride in mixtures of this gas with hydrogen, trustworthy results may be obtained by absorbing the gas in $N/2$-iodine solution, hypochlorite solution, hypobromite solution, concentrated potassium iodate solution, $N/1$-silver nitrate solution, mercuric chloride solution, and mercurous salt solutions. The following solutions may also be employed for the absorption provided that the residual hydrogen is treated with a reagent to remove volatile substances (chlorine, bromine, ammonia, etc.) introduced from the solution: chlorine water (containing not more than 0·16% of chlorine), saturated bromine water, acidified $N/5$-bromide-bromate solution, ammoniacal silver solutions, cuprous chloride containing hydrochloric acid, and acidified $N/2$-permanganate solution. A mixture of hydrogen and phosphorus hydride, such as is obtained by the action of potassium hydroxide on phosphorus, may be stored over saturated sodium chloride solution for a long time without undergoing any change; this solution is also used in the measuring burette. W. P. S.

Concentration Method for the Estimation of Small Quantities of Phosphoric Acid in Limestone. F. HINDEN (*Zeitsch. anal. Chem.*, 1915, **54**, 214—216).—Twenty-five grams of the powdered limestone are mixed with 100 c.c. of water, 120 c.c. of dilute nitric acid (1 : 1) are added, the mixture is boiled for ten minutes, the insoluble portion being then separated by filtration, and washed. The filtrate is heated to boiling, and ammonia is added until the solution just becomes turbid, owing to the precipitation of iron and aluminium hydroxides (if the limestone does not contain iron, a small quantity of ferric chloride should be added); 0·5 gram of calcium carbonate is now added, the mixture boiled for five minutes, and the precipitate, consisting of calcium carbonate, ferric carbonate, and aluminium hydroxide, and containing the whole of the phosphoric acid, is collected, washed, and then dissolved in dilute nitric acid. This solution is evaporated to dryness, silica is separated by filtration, and the phosphoric acid in the filtrate is estimated by the molybdate method.

W. P. S.

Analysis of Granules of Arsenious Acid and of Sodium Arsenate. M. FRANÇOIS and E. LASAUSSE (*J. Pharm. Chim.*, 1915, [vii], **11**, 226—237).—In the case of arsenious acid, the granules (at least 50, preferably 100) are counted, weighed, and heated in a conical flask, on a water-bath, for three hours with 20 c.c. of nitric acid (D 1·38). It is then diluted with 20 c.c. of water, made alkaline with strong ammonia, and filtered if necessary. Magnesia mixture (20 c.c.) and ammonia (20 c.c.) are then added, and the solution left for three days. The precipitate of ammonium magnesium arsenate is washed by decantation, collected on a filter, dried at 100°, and weighed.

As sodium arsenate contains less arsenic, it is necessary to employ at least 100 granules, which are heated with 40 c.c. of nitric acid. Otherwise, the method is the same as for arsenious acid granules. N. H. J. M.

Detection and Estimation of Arsenic in Organic Compounds and in Mixtures Containing Organic Matter. L. BARTHE (*Bull. Soc. pharm. Bordeaux*, 1914, 340; from *J. Pharm. Chim.*, 1915, [vii], **11**, 245—246).—Bressanin's reaction seems to be as sensitive as that employed by Bougault. In toxicological examinations, it is desirable to destroy the organic matter by heating the substance (0·5 gram) for two hours only with strong sulphuric acid (25—30 c.c.). N. H. J. M.

Estimation of Boron in Iron. J. M. LINDGREN (*J. Amer. Chem. Soc.*, 1915, **37**, 1137—1139).—The method of estimating boric acid described by Wherry (A., 1909, ii, 92) has been applied to the estimation of small quantities of boron in iron.

The iron is dissolved in a mixture of equal parts of concentrated hydrochloric and nitric acids and water, and the iron is precipitated by means of calcium carbonate. The precipitate is collected, mixed with asbestos fibre in order to facilitate washing, washed eight or ten times with hot water, and the filtrate titrated with 0·1*N*-alkali hydroxide in presence of mannitol and phenolphthalein. The method gives satisfactory results. E. G.

The Detection of Carbon Dioxide, Especially in a Mixture of Carbonate and Sulphite. JULIUS PETERSEN (*Zeitsch. anorg. Chem.*, 1914, **88**, 234—236).—The substance is placed in a vessel with delivery tube, and is covered with hydrochloric acid, a little zinc being added. The hydrogen carries the other gases with it into the absorbing apparatus. The first washing flask contains 3% hydrogen peroxide, and the second lime-water. For mixtures which evolve chlorine, potassium iodide is used in place of hydrogen peroxide. C. H. D.

Carbonic Acid in Mineral Waters Considered from the Analytical Standpoint. RAMÓN LLORD Y GAMBOA (*Anal. Fis. Quim.*, 1915, **13**, 238—252).—A review of the methods employed in the estimation of carbon dioxide in mineral waters, and a discussion of the results obtained in specific instances. A. J. W.

Estimation of Carbon Dioxide in Baking Powder and Carbonates. H. W. BRUBAKER (*J. Ind. Eng. Chem.*, 1915, **7**, 432—433).—The carbon dioxide is liberated from the baking-powder by treating the latter with saturated sodium chloride solution, and the gas is collected and measured over saturated sodium chloride solution. In the estimation of carbon dioxide in carbonates, the decomposition of the carbonate is effected by hydrochloric acid saturated previously with carbon dioxide, in order to obviate any correction for the quantity of gas dissolved by the acid. W. P. S.

Estimation of Carbonic Acid in Self-Raising Flours and Baking Powders. T. MACARA (*Analyst*, 1915, **40**, 272—275).—For the valuation of baking-powders and similar preparations, the author suggests that the "apparent" available carbon dioxide should be estimated, and he defines this as the amount of carbon dioxide evolved on boiling with water for thirty minutes, that is, the carbon dioxide liberated by the action of the acid ingredient of the powder, together with 25% of the carbon dioxide present in the excess of sodium hydrogen carbonate (when boiled with water for thirty minutes, sodium hydrogen carbonate yields 25·58% of the total carbon dioxide present). For the estimation, 5 grams of the baking-powder are treated in a flask with 100 c.c. of alcohol, 100 c.c. of water, and 100 c.c. of liquid paraffin, a few pieces of pumice are added, and the mixture is boiled for fifteen minutes, the liberated carbon dioxide being absorbed in an excess of barium hydroxide solution; 500 c.c. of boiling water are then added to the flask, the boiling is continued for a further fifteen minutes, the excess of barium hydroxide is neutralised, and the barium carbonate titrated. W. P. S.

Estimation of the Composition of Mixtures of Argon and Nitrogen by means of Liquid Air. L. HAMBURGER and H. FILIPPO IZN (*Zeitsch. angew. Chem.*, 1915, **28**, 75—76).—The method depends on a measurement of the difference in vapour pressure of pure argon and the nitrogen-argon mixture in a sort of differential vapour-pressure thermometer, the bulbs of which communicate at the base with a mercury reservoir, and at the apex are drawn out into narrow tubes, leading through a mercury seal to two fine metal tubes immersed in liquid air. One of the bulbs is permanently filled with pure argon, the other is connected through a three-way tap to a high vacuum pump and to the nitrogen-argon gas-holder through a glass spiral placed in a cooling bath at about $-80°$ to condense water vapour, etc. After this bulb has been exhausted, the gas is let in, and partial condensation occurs in the metal tubes cooled by the liquid air. A difference in level of the mercury in the two bulbs of the thermometer results, proportional to the amount of argon in the mixture. The apparatus is calibrated by making observations with gaseous mixtures of known argon content, and subsequent estimations can be relied on to an accuracy of 0·5%, which is quite sufficient for purposes of works' control. G. F. M.

Practical Methods for the Estimation of Radium. I. Interchangeable Electroscope and its Use. S. C. LIND (*J. Ind. Eng. Chem.*, 1915, **7**, 406—410).—The instrument described is constructed in two easily detachable parts; the upper part, consisting of the telescope and leaf electroscope, may be transferred to any number of discharge chambers. The latter consist essentially of a brass cylinder provided with glass taps at the top and bottom, and contain a brass electrode suspended from a rod which is screwed through the top and touches a spring connected with the leaf system. The upper part of the apparatus comprises a brass cylinder containing the leaf system; the ends of this cylinder are closed by mica sheets, inside which are iron gauze sheets to carry off any stray electrical discharge. A charging device for the electroscope is fitted at the side of the cylinder, whilst the telescope screws into one end of the latter. The original should be consulted for the exact details of construction of the apparatus.

W. P. S.

Separation of the Alkaline-earth Metals and the Alkalis. ROBERT GILMOUR (*Chem. News*, 1915, **111**, 217).—The following method is suggested for the qualitative analysis of the metals of groups IV and V. From the solution of the carbonates of barium, strontium, and calcium in acetic acid, barium is removed by the addition of potassium chromate. From the filtrate, strontium and calcium are reprecipitated as carbonates by the addition of ammonium carbonate, and again dissolved in acetic acid. After rendering alkaline with ammonia, the solution, which should not occupy more than 4—5 c.c., is divided into two parts. In the one, strontium is detected by the addition of calcium sulphate, and in the other the presence of calcium is manifested by the white precipitate of calcium potassium ferrocyanide, obtained by adding an equal volume of saturated potassium ferrocyanide solution, strontium giving no such precipitate. In the group IV filtrate, magnesium is detected by adding, after concentration to 10 c.c., 5 c.c. ammonium carbonate and 15 c.c. alcohol, when a precipitate of $MgCO_3,(NH_4)_2CO_3$ forms after some minutes. Sodium and potassium are detected in the filtrate in the usual way.

G. F. M.

Water Analysis. Rapid Estimation of Magnesium in Presence of Calcium by Titration. VICTOR FROBOESE (*Zeitsch. anorg. Chem.*, 1914, **89**, 370—376).—Two hundred c.c. or more of the water are heated to boiling, a drop of methyl-orange is added, and slightly more than the necessary quantity of concentrated oxalic acid solution, followed by sufficient 50% potassium hydroxide to change the colour to yellow. The liquid should become red again on cooling. Five drops of phenolphthalein solution are then added, followed by sufficient *N*/10-potassium hydroxide to produce a slight pink coloration. This end-point must be reached exactly, if necessary by repeating. The liquid is now titrated with *N*/10-potassium palmitate (Blacher,

Grünberg and Kissa, A., 1913, ii, 153) until the colour is distinctly pink. The exact neutralisation must be carried out immediately before the titration with palmitate.

Many analyses are given. C. H. D.

Separation of Magnesium from Lithium by means of Ammonium Carbonate in Alcoholic Solution. J. Gray Dinwiddie (*Amer. J. Sci.*, 1915, [iv], **39**, 662—664).—The magnesium is precipitated from its 50% alcoholic solution by means of ammonium carbonate. Twenty-five c.c. of an aqueous solution containing magnesium and lithium chlorides are mixed with 25 c.c. of 93% alcohol, and 50 c.c. of an alcoholic ammonium carbonate solution are added (this solution is prepared by mixing 1500 c.c. of saturated aqueous ammonium carbonate solution with 300 c.c. of concentrated ammonia and 1900 c.c. of 93% alcohol, and filtering off the precipitated ammonium carbonate). The precipitate is then collected, redissolved in the minimum quantity of hydrochloric acid, the solution is diluted to 10 c.c., and treated with 15 c.c. of alcohol and 50 c.c. of the ammonium carbonate solution. The precipitate now obtained is collected, washed with the ammonium carbonate solution, ignited, and weighed as magnesium oxide.

W. P. S.

Method for the Estimation of Copper in Commercial Copper Sulphate. Georg Incze (*Zeitsch. anal. Chem.*, 1915, **54**, 252—255).—The copper sulphate solution is treated with an excess of thiosulphate solution containing thiocyanate; the copper sulphate is thus reduced and precipitated as cuprous thiocyanate, and the excess of thiosulphate is then titrated. The reactions proceed according to the equations

$$8CuSO_4 + Na_2S_2O_3 + 5H_2O = 4Cu_2SO_4 + Na_2SO_4 + 5H_2SO_4$$

and $4Cu_2SO_4 + 8NH_4CNS = 8CuCNS + 4(NH_4)_2SO_4$. The thiosulphate solution is prepared by dissolving 19·878 grams of the salt and 8 grams of ammonium thiocyanate in 1 litre of water; the iodine solution used for the titration of the excess of the thiosulphate contains 1·0178 gram of iodine and 5 grams of potassium iodide per litre. Ten grams of the copper sulphate are dissolved and diluted to 500 c.c.; 50 c.c. of this solution are treated with 52 c.c. of the thiosulphate solution, starch solution is added, and the mixture titrated with iodine solution. The percentage quantity of copper sulphate in the sample is found by deducting 20 from the number of c.c. of iodine solution required for the titration, and dividing the remainder by 5. The presence of iron salts in the copper sulphate does not interfere with the estimation.

W. P. S.

Separation of Manganese as Manganous Sulphide from Alkali and Alkaline-earth Metals. V. M. Fischer (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1519—1526).—The separation of manganese as sulphide by precipitation with an alkali sulphide in

presence of ammonia and ammonium chloride is attended with difficulty, the precipitate being usually amorphous, troublesome to filter and wash, and readily oxidisable in the air. Conversion of the precipitate by prolonged boiling into the green form, which is easily manipulated and does not undergo oxidation, may be accompanied by precipitation of the alkaline-earth metals as carbonates as a result of absorption of carbon dioxide from the air. The methods recommended for obtaining the green sulphide without heating the solution are uncertain in their results. The author, having determined the conditions under which the green sulphide may invariably be obtained in the cold (this vol., ii, 462), gives the following method for separating manganese as sulphide from solutions containing metals of the alkalis and alkaline earths.

To 100—200 c.c. of the liquid are added 5—15 grams of ammonium chloride and 50—60 c.c. of ammonia solution (D^{16} 0·895); the solution should remain perfectly clear. From a dropping funnel with an orifice 0·75 mm. in diameter, 50—100 c.c. of ammonium hydrogen sulphide solution, freshly prepared from 2·5% ammonia solution, are slowly added, the addition occupying ten to fifteen minutes, and the vessel being meanwhile constantly and vigorously shaken. Conversion of the flesh-coloured manganese sulphide into the green variety proceeds during the addition of the precipitant, and, when it is not immediately completed, the Erlenmeyer flask should be corked; the change occupies from a quarter to one and a-half hours, according to the proportion of ammonium chloride present and the rapidity of the precipitation. When all the precipitate is green, the liquid is diluted to 500—700 c.c. with cold, recently boiled water, and filtered. The precipitate is washed with dilute ammonium hydrogen sulphide solution containing a little ammonium chloride, and is subsequently either heated with sulphur in a current of hydrogen and weighed as sulphide, or dissolved in dilute hydrochloric acid and converted into phosphate. This method yields very accurate results, and, as it is not affected by the presence of ammonium acetate, it is applicable after the removal of the iron by the acetate method.

When sufficient ammonia is present, and the precipitation is effected slowly, it becomes unnecessary to convert the rose-coloured into the green sulphide, since the former is then obtained in a dense form, which can be readily filtered and washed, and does not undergo oxidation. In this case, the following quantities should be used: 150—200 c.c. of solution, 5—10 grams of ammonium chloride, 50—75 c.c. of ammonia solution, and 75—100 c.c. of the cold ammonium hydrogen sulphide solution. When diluted with 500—1000 c.c. of cold, boiled water, the precipitate usually settles rapidly, leaving the supernatant liquid clear; filtration, etc., may then be carried out immediately. If, however, the liquid remains turbid, the precipitate is allowed to change into the green form before filtration. Either procedure gives excellent results, which are not affected by the presence in the solution of hydroxylamine hydrochloride (*loc. cit.*).

Preliminary experiments indicate that a modification of the

above method of precipitating manganous sulphide may be employed in the microchemical estimation of manganese.

T. H. P.

Apparatus for the Reduction of Iron Solutions by Metallic Aluminium. C. L. SCHUMANN (*J. Ind. Eng. Chem.*, 1915, **7**, 431).—For the reduction of ferric salt solutions, a piece of aluminium chain made from heavy aluminium wire may be employed; the chain is attached to a length of glass rod, so that it may be removed from the solution when reduction is completed. The chain should be weighed before and after use in order that a correction may be made for the amount of iron present in the aluminium.

W. P. S.

New Sensitive Reaction for, and a Colorimetric Method of Estimating, Iron. L. A. TSCHUGAEV and B. P. ORELKIN (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1874—1876; *Zeitsch. anorg. Chem.*, 1914, **89**, 401—404).—This reaction depends on the formation of a coloured oximine when a solution containing a ferrous compound is treated with dimethylglyoxime, α-benzildioxime, etc. (A., 1905, i, 743). With ferric salts, or even with very dilute solutions of ferrous salts, a reducing agent is required, hydrazine being the most suitable for this purpose. To the solution to be tested for iron in the ionic condition are added, successively, a small quantity of hydrazine sulphate, excess of ammonia solution, and an alcoholic solution of dimethylglyoxime. The solution is heated to boiling and then cooled. A faint, but distinct, rose-red coloration is obtained in presence of 1 part of iron per 100,000,000 of solution. The presence of alkali metals and magnesium in amount one hundred times that of the iron does not interfere with the reaction, which is, however, diminished greatly in sensitiveness by aluminium or zinc.

For the estimation of the iron, the procedure is as follows. One hundred c.c. of the solution, mixed with 1 gram of hydrazine sulphate and 5 c.c. of saturated, alcoholic dimethylglyoxime solution, are heated to boiling in a round flask, and 10 c.c. of 25% ammonia solution then added. The liquid is next boiled for thirty seconds, and afterwards rapidly cooled under the tap. A test solution containing a known proportion of iron is treated in an exactly similar manner, the two solutions being then made up to a definite volume, say 125 c.c., and compared in the colorimeter in the usual way.

This method admits of the estimation of 0·1—1 mg. of iron with an accuracy of 0·5%; when the iron is accompanied by the hundredfold quantity of magnesium, the error of the estimation does not exceed 1%.

T. H. P.

Estimation of Free Acid and of Oxychloride (in Ferric Chloride Solution). G. ROMIJN (*Amer. J. Pharm.*, 1915, **87**, 245—248).—Two c.c. of the ferric chloride solution are added to 50 c.c. of water containing 0·5 gram of a mixture consisting of

1 gram of cupric chloride and 49 grams of soluble starch, and $N/1$-thiosulphate solution is added (5·5 c.c. for the U.S.P. ferric chloride solution and 9 c.c. for that prescribed in the Netherlands Pharmacopœia). Methyl-orange is now added; if the mixture shows an acid reaction it is titrated with $N/10$-sodium hydroxide solution; if alkaline, the test is repeated after the addition of 1 c.c. or more of $N/10$-hydrochloric acid to the ferric chloride solution before the other reagents are introduced. The author is of opinion that 2 c.c. of ferric chloride solution should require not more than 1·2 c.c. of $N/10$-sodium hydroxide solution; if the solution is alkaline in reaction, the addition of 1 c.c. of $N/10$-hydrochloric acid should render it acid. W. P. S.

Ferrous Sulphate Method for the Estimation of Vanadium in Steel. GEORGE T. DOUGHERTY (*J. Ind. Eng. Chem.*, 1915, **7**, 419—420).—A quantity of 2—4 grams of the drillings is boiled with 60 c.c. of water and 10 c.c. of concentrated sulphuric acid, 40 c.c. of nitric acid (D 1·2) are then added, and the solution is boiled for ten minutes. After cooling, 60 c.c. of dilute sulphuric acid are added, the mixture is diluted to 450 c.c., 3 c.c. of 1% potassium ferricyanide solution are added as indicator, and the solution is titrated with $N/20$-ferrous ammonium sulphate solution; 0·4 c.c. is deducted from the quantity of ferrous ammonium sulphate solution used. This correction is independent of the weight of the sample taken, the presence of chromium, and of the carbon content up to 0·5%. In the case of steels containing more than 0·5% of carbon, the method is modified by treating the solution, immediately after the boiling with nitric acid, with 60 c.c. of dilute sulphuric acid and 5—8 grams of ammonium persulphate; the mixture is boiled for fifteen minutes, cooled, and titrated as described. Under these conditions, the correction is 0·5 c.c. for steels containing 0·6—0·7% of carbon, and 0·6 c.c. for 0·9—1·25% of carbon. W. P. S.

Estimation of Quinquevalent Vanadium by means of Sodium Thiosulphate. G. O. OBERHELMAN (*Amer. J. Sci.*, 1915, [iv], **39**, 530—534).—Vanadic acid may be titrated with sodium thiosulphate solution, the reaction proceeding according to the equation: $V_2O_5 + 2Na_2S_2O_3 + 2HCl = V_2O_4 + Na_2S_2O_6 + 2NaCl + H_2O$. Trustworthy results are, however, obtained only under the following conditions as to concentration of acid, excess of thiosulphate, etc. The vanadate solution is diluted to 400 c.c., 5 mg. of crystallised copper sulphate and 1·5 c.c. of 32% hydrochloric acid are added, and $N/10$-thiosulphate is run in, with constant stirring, until an excess of 7·5 c.c. is present. After some time, and when the colour of the solution has changed to sky-blue, potassium iodide is added in the proportion of 0·1 gram for each 100 c.c. of solution, and the excess of thiosulphate is titrated with $N/10$-iodine solution, using starch as indicator. When the amount of vanadate to be estimated is not known, a preliminary titration, using 20 mg.

of copper sulphate, will give information as to the proper adjustment of the excess of thiosulphate needed in the actual estimation.
W. P. S.

Estimation of Columbium in Presence of Tantalum, and some Reactions of Tantalum Compounds. ARTHUR G. LEVY (*Analyst*, 1915, **40**, 204—217).—A volumetric method for the estimation of columbium is described, and is based on the fluoride method of Osborne (A., 1886, 393). The mixed oxides of columbium and tantalum are dissolved in 7 c.c. of hydrofluoric acid, the solution evaporated to dryness, and the residue fused. The mass is transferred to a flask with the aid of 20 c.c. of water, 40 c.c. of hydrochloric acid are added, the columbium reduced by the addition of 10 grams of zinc, the solution then diluted with a mixture of 270 c.c. of water, 10 c.c. of sulphuric acid and 20 c.c. of a saturated sodium phosphate solution, and titrated with $N/10$-potassium permanganate solution. The reduction only goes as far as an oxide, $Cb_{10}O_{17}$, and each c.c. of $N/10$-permanganate solution is equivalent to 0·00834 gram of Cb_2O_5. It is shown that large losses of tantalum are caused by dissolving tantalum oxide in hydrofluoric acid and igniting the residue obtained on evaporating the solution to dryness, by igniting potassium tantalum fluoride with excess of potassium fluoride, and by igniting mixtures of tantalum oxide and ammonium fluoride. W. P. S.

The Analysis of Platinum. F. MYLIUS and A. MAZZUCCHELLI (*Zeitsch. anorg. Chem.*, 1914, **89**, 1—38).—For the purification of platinum, conversion into sodium platinichloride is recommended. The salt contains an excess of sodium chloride, which is removed by drying at 120°, and dissolving in two parts of cold, absolute alcohol, in which the chloride is insoluble. By filtering into a volume of water equal to 15% of the alcohol, the platinichloride is precipitated as pure crystals, $Na_2PtCl_6,6H_2O$. The small quantity in solution is recovered by evaporation after acidifying with hydrochloric acid. The salt may be heated in hydrogen or reduced by means of pure hydrazine hydrochloride.

The qualitative reactions of the six platinum metals, in solutions containing 1 gram of metal per litre as chloride, are tabulated. The colour of the solutions is compared with that of other chlorides. A complete scheme of qualitative separations is described, comprising the six platinum metals, with silver, gold, copper, and iron.

The quantitative procedure is different for commercial and highly purified platinum. In order to distinguish the two classes, 0·1 gram of the metal is dissolved and evaporated to dryness with 0·1 gram of sodium chloride, dissolved in 10 c.c. of water, and heated with about 0·02 gram of sodium carbonate. After cooling, one or two drops of sodium hypochlorite solution are added, and the solution is again warmed. Should the solution remain clear orange-yellow, the metal is highly purified, whilst the commercial quality yields a dark solution, which deposits a bluish-black precipi-

tate. This precipitate contains practically the whole of the impurities, including the gold, which is not precipitated when alone. The same method may be applied to that portion of a platinum ore which is soluble in aqua regia.

For an approximate analysis of commercial platinum, 10 grams of metal suffice, but for an accurate analysis of the purified metal as much as 100 grams must be used. Silica vessels are used for solution, and the precipitation by sodium hypobromite is performed in a platinum basin. After collecting this precipitate, the filtrate is boiled with alcohol, when a further small precipitate may be obtained. A complete scheme of separation is given. The precipitate of oxides is dissolved, precipitated as ammonium double chlorides, and gold and copper precipitated from the filtrate as sulphides. Rhodium is left in the sulphide filtrate, and estimated colorimetrically. If present in larger quantities, the rhodium, after separation, always contains iridium. Iron is also present in this solution, and is precipitated as hydroxide, and nickel or cobalt as sulphide.

The double ammonium chlorides are strongly ignited, and digested with a mixture of 1 part of aqua regia and 3 parts of water. Nearly all the iridium remains in the residue. Palladium is precipitated from the solution as sulphide. Ruthenium, if present, is in the iridium residue, which may be fused with potassium hydroxide and nitrate in a gold crucible. The solution in water deposits blue iridium oxide; ruthenium, indicated by a green coloration, is estimated by treatment with sodium hypochlorite and distillation in chlorine.

For purified platinum, the sodium platinichloride is repeatedly recrystallised from a 1% solution of sodium carbonate. The mother liquor, after removal of 95 to 99% of the platinum, may be treated as above, or ammonium chloride may be added to remove the remaining platinum, with some iridium, the other impurities being precipitated by passing hydrogen sulphide through the hot solution for several hours. Heraeus' purified platinum contains about 0·01% of total impurities. C. H. D.

Separation of Palladium from Tin by Electrolytic Deposition of the Palladium. A. Gutbier, C. Fellner, and R. Emslander (*Zeitsch. anal. Chem.*, 1915, **54**, 208—213).—A solution containing the two metals is poured into a mixture of 25 c.c. of 2*N*-sulphuric acid and 500 c.c. of water; after some time, the mixture is heated at 65°, and submitted to electrolysis at this temperature. A current of 1·25 volt and 0·25 ampere is employed; the cathode consists of a semicircular piece of platinum gauze, and a platinum spiral forms the anode. The electrolyte is stirred by a glass screw placed between the electrodes, and rotated at 2400 revolutions per minute. After the palladium has been deposited, the solution is boiled with the addition of ammonium nitrate, and the tin oxide collected (compare Amberg, A., 1904, ii, 593; Wohler and Sprengel, A., 1911, ii, 338). W. P. S.

Separation of Palladium from Tin by means of Dimethylglyoxime. A. GUTBIER and C. FELLNER (*Zeitsch. anal. Chem.*, 1915, **54**, 205—208).—The method depends on the precipitation of palladium from its acid solution by dimethylglyoxime; tin salts do not yield an insoluble compound with this reagent. The metals are dissolved in aqua regia, and the solution, containing hydrochloric acid, but no free chlorine, is diluted to 150 c.c., heated on a water-bath, and treated with a 1% dimethylglyoxime solution. The heating is continued for one hour after the precipitate has settled and the addition of more of the reagent produces no further turbidity; the mixture is then cooled, the precipitate collected on a filter, washed with dilute (not more than 2%) hydrochloric acid, dried, and ignited at first in contact with air and then in an atmosphere of hydrogen. The tin may be estimated in the filtrate. W. P. S.

Estimation of Methyl Alcohol in Presence of Ethyl Alcohol. G. CECIL JONES (*Analyst*, 1915, **40**, 218—221).—In the modification of Denigés' method, described by Simmonds (A., 1912, ii, 208), small variations in the experimental conditions have a decided effect on the results obtained. The method is, however, capable of detecting the presence of 0·1% of methyl alcohol in ethyl alcohol, and of estimating proportions of about 1% with an error not exceeding 1 part in 20 if 5 c.c. of 2% potassium permanganate solution are used for the oxidation in place of the 2·5 c.c. prescribed by Simmonds. The quantity of sulphuric acid added with the permanganate, within the limits 0·1 and 0·3 c.c., is of little effect, but the subsequent addition of acid must be as nearly as possible the same in any one set of experiments. The composition of the Schiff's reagent is of importance; it should be prepared by dissolving 0·2 gram of magenta-base in 10 c.c. of freshly made, saturated sulphur dioxide solution, and, after twenty-four hours, diluting the solution to 200 c.c. Five c.c. of the reagent are used for each test; if the quantity is increased to 10 c.c., the acid concentration is so much reduced that even acetaldehyde from ethyl alcohol develops a coloration.

W. P. S.

Estimation of Certain Groups in Phosphatides. MARY LOUISE FOSTER (*J. Biol. Chem.*, 1915, **20**, 403—413).—The proportion of glycerol in lecithin and other phosphatides is estimated by heating the substance in a Zeisel apparatus with ammonium iodide and hydriodic acid at 120° in a paraffin bath, whereby *iso*propyl iodide is quantitatively evolved, and is estimated by alcoholic silver nitrate in the usual way. If alkyl groups are also present in the phosphatide, raising the temperature to 180—190° leads to their evolution as methyl or ethyl iodide, but trials with choline chloride showed that the reaction is not quantitative. The method affords a means of differentiating between the glycerol and alkyl groups of phosphatides, and indicates, for ex-

ample, the absence of methyl or ethyl groups in kephalin, which is in harmony with MacArthur's observations on the absence of choline and neurine in the kephalin molecule (A., 1914, i, 1197).

H. W. B.

Bromine Method of Estimating Phenol. W. Versfeld (*Analyst*, 1915, **40**, 281—283).—The phenol solution is titrated with a hypobromite solution, prepared by saturating 250 c.c. of $N/5$-sodium hydroxide solution with bromine, boiling the mixture to expel the excess of bromine, and diluting it to 1 litre; 100 c.c. of this solution are used for each 1 c.c. of 5% phenol solution or its equivalent. For the estimation, the phenol solution, containing approximately 0·05 gram of phenol, is placed in a 1000 c.c. stoppered flask, and 50 c.c. of water are added, followed by 5 c.c. of concentrated hydrochloric acid and 100 c.c. of the hypobromite solution. After fifteen minutes, 20 c.c. of 10% potassium iodide solution are added; this is allowed to react for five minutes, the mixture then diluted to 400 c.c., and the liberated iodine is titrated with $N/10$-thiosulphate solution. A control is made at the same time, using the quantities of reagent mentioned, but without the phenol. The difference between the number of c.c. of $N/10$-thiosulphate solution used in the control and the test multiplied by 0·156746 gives the percentage quantity of phenol in the solution if 1 c.c. of the latter was taken for the estimation. W. P. S.

Mutarotation of Phenylosazones of Pentoses and Hexoses. P. A. Levene and F. B. La Forge (*J. Biol. Chem.*, 1915, **20**, 429—431).—The melting points of the purified osazones at a rate of heating of about four to five seconds per 1° are as follows: altrose 178°, *l*-arabinose 166°, galactose 201°, dextrose 208°, gulose 168°, *d*-xylose 164°, all with decomposition at the same, or slightly higher, temperature. The optical rotations of the same osazones in Neuberg's pyridine–alcohol mixture (0·1 gram of substance in 5 c.c.), measured (i) soon after the preparation of the solution, and (ii) after twenty-four hours, have also been determined: altrose, (i) −0·40, (ii) −0·29; *l*-arabinose, (i) +0·55, (ii) +0·30; galactose, (i) +0·80, (ii) +0·34; dextrose, (i) −0·62, (ii) −0·35; gulose, (i) +0·07, (ii) +0·50; *d*-xylose, (i) −0·09, (ii) −0·43. All the observations were made in a 0·5-dcm. tube with sodium light. H. W. B.

Volumes Occupied by Standard Solutions at Different Temperatures. H. Pellet (*Ann. Chim. anal.*, 1915, **20**, 97—99).—Ordinary volumetric solutions, and also sugar solutions containing up to 15% of sugar, have a coefficient of expansion which is approximately the same as that of water. The following are the volumes occupied by distilled water at various temperatures: at 4°, 1000·00 c.c.; at 10°, 1000·26 c.c.; at 15°, 1000·85 c.c.; at 20°, 1001·75 c.c.; at 25°, 1002·95 c.c.; at 30°, 1004·25 c.c.; at 35°, 1005·83 c.c. W. P. S.

Extension of the Sugar Reduction-Table. N. Schoorl (*Chem. Weekblad*, 1915, **12**, 481—482. Compare A., 1912, i, 750).—A table showing the reducing power of galactose, mannose, arabinose, xylose, and rhamnose towards Fehling's solution.

A. J. W.

Detection of Small Amounts of Sugar by Formation of Formaldehyde and the Substances in the Urine which Form Formaldehyde. E. Salkowski (*Zeitsch. physiol. Chem.*, 1915, **93**, 432—446).—The method described permits the detection with certainty of 0·2% dextrose in urine. After a preliminary treatment with lead acetate, the dextrose is precipitated from the urine by excess of lead acetate and ammonia. The precipitate is dissolved in hot acetic acid, and the dextrose oxidised to formaldehyde by potassium permanganate in sulphuric acid solution (see Rosenthaler, A., 1914, i, 249). Leach's test, as modified by Salkowski (this vol., ii, 190), is then applied. Attempts to simplify the procedure were unsuccessful.

Potassium permanganate in acid solution produces formaldehyde from creatinine and other, unrecognised substances in normal urine, but not from urea, uric acid, or purine bases. H. W. B.

Colorimetric Method for the Detection of Oxalic Acid and Manganese. J. F. Sacher (*Chem. Zeit.*, 1915, **39**, 319).—When a manganous salt solution is treated with a drop of sodium hydroxide solution, and oxalic acid solution is then added slowly, a red coloration is obtained at the moment when sufficient of the acid has been added to dissolve the manganese hydroxide. The reaction proceeds in the cold, and is not due to the formation of permanganate. The oxalic acid must not contain reducing substances or tannin, but the reaction takes place in the presence of sulphates, nitrates, phosphates, acetates, citrates, tartrates, lactates, benzoates, salicylates and formates; only small quantities of formates should, however, be present. The test will detect the presence of 1 part of oxalic acid in 5000 parts of solution, or 1 part of manganese in 200,000. W. P. S.

Estimation of Resins in Hops. J. Schmidt, O. Winge, and J. P. H. Jensen (*Compt. rend. Lab. Carlsberg*, 1914, **11**, 116—147).—The γ-resin of hops is not valueless, as hitherto supposed; it gives a taste to the wort, and helps the precipitation of the proteins.

The resins of hops which are soluble in cold ethyl ether are not equally bitter, the relation between the bitterness of the different resins being in the proportion $\alpha : \beta : \gamma = 10 : 7 : 4$. The total resin thus extracted, and estimated by titration, indicates approximately, however, the bitterness value of the hops.

Methods hitherto employed, in which so-called soft resins are separated from the hard resin, give misleading results.

In the method now employed, about 5 grams of pulverised hops (=about 25 c.c.) are transferred to a weighed 300 c.c. Erlenmeyer

flask, dried for twenty-four hours in a vacuum at 35°, cooled over sulphuric acid, and again weighed. It is then treated with 150 c.c. of dry ether free from alcohol, and frequently shaken during an hour. It is then filtered, washed with about 100 c.c. of ether, and titrated with 0·05*N*-potassium hydroxide in 93% alcohol, using six to eight drops of a 1% solution of phenolphthalein in 93% alcohol. The amount of resin is calculated by dividing twice the number of c.c. of 0·05*N*-alkali required by the dry weight of the hops. N. H. J. M.

Recent Advances in the Analysis and Evaluation of Rubber and Rubber Goods. PHILIP SCHIDROWITZ (*Analyst*, 1915, **40**, 223—233).—A synopsis of the recent literature concerning the chemical and physical examination of caoutchouc and its manufactured products. The points dealt with in the case of crude caoutchouc are: composition, resins, nitrogenous substances, impurities, estimation of caoutchouc, estimation of moisture, physical and mechanical tests, vulcanisation tests, etc. Under vulcanised rubber, papers dealing with analysis, separation of minerals, starch, fibres, etc., estimation of sulphur and caoutchouc, and the examination of rubber goods, are discussed. W. P. S.

Reactions of Strophanthin from Strophanthus Kombé and Strophanthus Gratus. C. REICHARD (*Pharm. Zentr.-h.*, 1915, **56**, 159—163, 174—178).—The strophanthin obtained from *Strophanthus Kombé* is an amorphous, yellow powder, whilst that from *S. Gratus* occurs as colourless crystals. The former dissolves readily in 90% sulphuric acid, whilst the latter dissolves with difficulty. When treated with concentrated sulphuric acid, *Kombé*-strophanthin yields an intense green coloration, but *Gratus*-strophanthin remains unaltered; on heating, both mixtures yield a green coloration, which, in the case of *Kombé*-strophanthin, changes to grey-blue if the heating is not continued. *Gratus*-strophanthin dissolves in warm potassium dichromate solution, and yellow crystals are deposited when the solution is cooled; *Kombé*-strophanthin behaves similarly, but the former crystals yield only a slight green coloration when treated with sulphuric acid, whilst the latter give a green coloration with dilute sulphuric acid. Reactions with many other reagents are also described. W. P. S.

Creatine and Creatinine Estimations. The Occurrence of Creatine. J. LUCIEN MORRIS (*J. Biol. Chem.*, 1915, **21**, 201—208).—Precipitation of creatinine as creatinine potassium picrate is recommended; this does away with the interfering action of acetone substances and dextrose, which comes into play when the colorimetric method is used. The identity of creatine in the urine of children, post-partum women, diabetes, and starvation is established. W. D. H.

General and Physical Chemistry.

An Apparatus for Projecting Spectra. H. Hartridge (*J. Physiol.*, 1915, **49**, 406—409).—The apparatus avoids some of the disadvantages of older methods; a spectrum of wide dispersion and of great intensity is obtained. Briefly, it is a combination of a right-angled prism of light crown glass with a celluloid replica diffraction grating mounted on the hypotenuse. W. D. H.

Measurements of Wave-length According to the International System in the Arc Spectrum of the Elements from Red to Infra-red (Lithium, Sodium, Potassium, Cæsium, Rubidium, Calcium, Strontium, Barium, Zirconium, Lanthanum, and Cerium). I. Josef Maria Eder (*Chem. Zentr.*, 1915, i, 1046).—The region of the spectrum investigated included the wave-lengths λ 6400 to λ 8500 Angström units, and the for the most part unknown lines of the above elements in this region were measured as far as the known visible spectra. For the photographic record extra rapid plates sensitised with dicyanin were employed, and the light was condensed by means of two crossed rock crystal cylindrical lenses into a narrow band on the slit of the spectrograph. By this means a relatively short exposure of three to twenty minutes was sufficient. G. F. M.

The Arc Spectrum of Gold According to the International Normals. Marie Quincke (*Zeitsch. wiss. Photochem*, 1915, **14**, 249—262).—Accurate measurements, recorded to 0·001 Å., have been made of the lines in the arc spectrum of gold between λ 6693 and λ 2352. The character and relative intensity of each line are indicated, and the wave-lengths compared with those given by previous observers. The data are discussed in reference to the possible occurrence of constant differences in frequency, but the result is inconclusive. H. M. D.

Measurements in the Arc Spectrum of Manganese According to the International Normals. Hans Fuchs (*Zeitsch. wiss. Photochem.*, 1915, **14**, 239—248, 263—280).—The wave-lengths of lines in the arc spectrum of manganese have been measured over the range λ 7070 to λ 2290. The relative intensities of the lines are indicated, and the wave-lengths, recorded to 0·001 Å., are compared with the values obtained by previous observers. H. M. D.

Measurements in the Spark Spectra of the Platinum Metals: Ruthenium, Rhodium, Palladium, Iridium, and Platinum in the Extreme Ultra-violet. Gustav Kail (*Chem. Zentr.*, 1915, **i**, 302—303; from *Sitzungsber. K. Akad. Wiss. Wien.*, 1914, **123**, II., A.).—A dispersion curve was plotted with the help of known lines for the quartz spectrograph used. The wave-lengths of the

shortest new lines measured for the platinum metals were: Rh, 1880·00 Ångström units; Ru, 1874·94; Pt, 1866·46; Pd, 1858·51; Ir, 1852·21. The total number of lines of the platinum metals in the extreme ultra-violet measured by the author was 1,071, of which 690 were previously unknown. The measurements are given in tabular form. H. W.

Observations on the Effect of the Electric Yield on the Spectral Lines. Sharp Separation of the Hydrogen Lines. J. STARK (*Chem. Zentr.*, 1915, i, 592; *Nachr. K. Ges. Wiss. Göttingen*, 1914, 427—444).—The lack of sharpness of the hydrogen lines separated by the influence of an electric field (A., 1914, ii, 315) suggested that a separation into further components might be possible with stronger fields. Using an electrostatic field of 104,000 volts per cm., this was found to be the case. The intensities of the individual components lay within much wider limits than in the Zeeman effect, and their darkening effects were not, therefore, all measured on the same plate, but the weakest and the strongest on two different plates, the intermediate lines serving for comparison. The distance between the components of each of the hydrogen lines, H_α, H_β, etc., is proportional to the strength of the field. Several electrons are always concerned in the emission of even a single line of the series. G. F. M.

Band Spectrum Associated with Helium. J. W. NICHOLSON (*Proc. Roy. Soc.*, 1915, [*A*], **91**, 432—439).—A mathematical paper in which evidence is brought in further support of Fowler's conclusion that the heads of the bands in the band spectrum of Goldstein and Curtis (A., 1913, ii, 539, 811) follow ordinary line-series laws. This mainly consists in showing that the doublet separations tend to zero at the limits of the series. Both the doublet series isolated by Fowler are strictly analogous to principal series in line spectra. The generalised Rydberg formula gives the most suitable representation of these series as well as of line series. J. F. S.

Application of Interference Methods to the Study of the Origin of Certain Spectrum Lines. THOMAS R. MERTON (*Proc. Roy. Soc.*, 1915, [*A*], **91**, 421—431).—It has been shown by Buisson and Fabry that by measuring the limiting order of interference at which fringes can be observed for different radiations, the mass of the particle emitting the radiations can be calculated if the temperature is known. In the case of radiations at low pressures the limiting order of interference at which fringes may still be visible is expressed by the relationship $N = K\sqrt{M}/T$, where N is the limiting order of interference, K a constant having a value $1{\cdot}22 \times 10^6$, M the atomic weight of the luminous particle, and T the absolute temperature. The author has carried out a number of experiments on the radiations from calcium, barium, strontium, argon, and helium. The method adopted consisted in throwing a beam of light from the source by means of a lens on to the plates of a Fabry and Perot sliding interferometer, and the ring systems

were focussed by means of an achromatic lens on to the slit of a Hilger constant deviation spectrometer. The interferometer plates were then slowly separated until a point was reached at which the fringes were only just visible. From the separation of the plates at this point the value of N can be calculated. Measurements were made both visually and photographically. It is shown that the g line of calcium is due probably to calcium molecules (Ca_2) of mass 80, whilst the H and K lines are due to calcium atoms. Strontium molecules are responsible for the line $\lambda=4607$, and barium molecules for the line $\lambda=5535$. It is also shown that the red spectrum of argon is due to atoms of mass 40, but the blue spectrum would appear to be due to particles of smaller mass; this result is probably to be explained by the presence of some cause other than the Doppler effect producing the broadening of the lines. The band spectrum of helium is also investigated.

J. F. S.

Enhanced Series of Lines in Spectra of the Alkaline Earths. W. M. Hicks (*Proc. Roy. Soc.*, 1915, [*A*], **91**, 451—463).—A theoretical paper in which the relationships of the S, D, and F series for calcium, strontium, barium, and radium are discussed.

J. F. S.

Dissociation Spectra in the Visible and Ultra-violet Portion. A. de Gramont (*Ann. Chim.*, 1915, [ix], **3**, 269—287).—A résumé of work already published (compare A., 1907, ii, 517; 1908, ii, 645; 1910, ii, 811; 1912, ii, 875; 1914, ii, 604). W. G.

Constitution of Organic Compounds in Relation to their Absorption of Light. E. C. C. Baly (*J. Soc. Chem. Ind.*, 1915, **34**, 393—399).—A paper read before the Liverpool section of the Society of Chemical Industry. Powerful arguments against Hantzsch's theories are developed, and the author shows how the variations in colour and absorption of the salts of acids or bases can be explained by his own views as to the field of force around the molecule. J. C. W.

The Ultra-violet Absorption of Certain Mono-derivatives of Benzene. Christine Strasser (*Zeitsch. wiss. Photochem.*, 1915, **14**, 281—311).—The ultra-violet absorption spectrum of the vapours of a number of mono-substituted derivatives of benzene has been examined. The wave-length data for the absorption bands exhibited by benzaldehyde, benzonitrile, benzyl alcohol, benzyl ethyl ether, and benzoic acid show that the spectra of these derivatives are similarly constituted. The chief bands fall into "longitudinal" series, which are characterised by a constant difference of frequency, the value of which varies from 94·0 to 97·0, according to the nature of the substituting atom or group. In addition, the spectra exhibit "lateral" series of bands, which differ in frequency from the bands of the "longitudinal" series by a constant amount. This "lateral" difference varies very markedly with the nature of the

substituent, its value for bromobenzene being 2·8 (compare following abstract), whilst for benzaldehyde it is 15·3 and for benzonitrile 23·6. The "lateral" differences for benzyl alcohol, benzyl ethyl ether, and benzoic acid could not be determined on account of the diffuseness of the bands, but by comparison of the results with those obtained by Witte it is evident that this difference depends essentially on the nature of the substituent. H. M. D.

Structure of the Ultra-violet Absorption Spectra of Benzene and its Mono-substituted Derivatives. Rudolf Witte (*Zeitsch. wiss. Photochem.*, 1915, **14**, 347—392).—Measurements have been made of the wave-lengths of the absorption bands in the spectrum afforded by the vapours of benzene, toluene, chlorobenzene, bromobenzene, aniline, phenol, and anisole. As a result of improvements in manipulative details it is claimed that the errors attaching to the recorded data are probably not greater than ±0·2 Å.U. The relative intensities of the bands have also been estimated, for it would seem that this factor is of special importance in the characterisation of the spectra in question.

The measurements indicate that the various spectra are of the same type. In all cases there are "longitudinal" series of bands which show a constant difference in frequency which varies only slightly, namely, from 92·2 for benzene to 96·4 for chlorobenzene. In addition to these bands, there are so-called "lateral" series, which differ in frequency from the members of the "longitudinal" series by a constant which varies considerably with the nature of the substituting atom or group. The values recorded for the lateral differences are: Cl, 3·3; CH_3, 3·1; Br, 2·8; NH_2, 15·7; OMe, 19·8; OH, 15·3. It is evident that these differences are highly sensitive to certain changes in the nature of the substituting group. Observations made with iodobenzene, nitrobenzene, and benzoic acid afford no evidence of selective absorption in these derivatives. H. M. D.

[Absorption Spectra.] The Mutual Influence of Hydroxyl and Carbonyl and Some Related Groups in the Ortho-position. H. D. Gibbs and D. S. Pratt (*Philippine J. Sci.*, 1913, **8**, 33—47).—In order to ascertain whether the relative reactivity of the carbonyl group in related compounds can be correlated with the position and persistence of ultra-violet absorption bands, the authors have investigated the absorption spectra of phenol, *o*-cresol, *o*-hydroxybenzyl alcohol, salicylic acid, and of the methyl ether of salicylic acid and methyl salicylate. The change in the spectrum brought about by the addition of alkali was also examined. The results are interpreted on the assumption that the absorption bands are to be ascribed to definite compounds.

For comparison, the absorption spectra of benzyl alcohol, benzyl acetate, benzyl methyl ether, benzyl chloride, and methyl benzoate were also examined. The first four of these show the same band ($1/\lambda = 3850$), which lies in the benzene region of the spectrum. The persistence of the band decreases in the order in which the substances are written. The absorption curve of methyl benzoate

is very similar, but it appears at greater dilution, and the head is shifted slightly towards the visible region ($1/\lambda = 3700$).

H. M. D.

Absorption Spectra of *o*- and *p*-Nitrophenols and *p*-Nitrosophenol. H. D. GIBBS and D. S. PRATT (*Philippine J. Sci.*, 1912, **7**, [*A*], 371—380).—Photographic records of the absorption spectra have been obtained in a series of experiments with 0·001 molar solutions, varying in thickness from 2 to 32 mm., and containing varying quantities of sodium ethoxide.

The band at 300 $\mu\mu$, which is exhibited by *p*-nitrophenol, shows no appreciable shift on the addition of alkali, but a new band makes its appearance at 405 $\mu\mu$. This band increases in persistence and breadth with the alkali concentration, whilst the band at 300 $\mu\mu$ is correspondingly reduced.

Similar changes are shown on the addition of sodium ethoxide to an alcoholic solution of *p*-nitrosophenol, the head of the band which makes its appearance in alkaline solution being at 410 $\mu\mu$.

In the case of neutral or acid solution of *o*-nitrophenol two bands are observed at 270 and 345 $\mu\mu$ respectively. The former is not greatly affected by the addition of alkali, but the latter gradually disappears, and a new band makes its appearance at 420 $\mu\mu$.

The authors consider that the observed facts are opposed to the theory put forward by Baly, Tuck, and Marsden (T., 1910, **97**, 571), and attribute the changes in the absorption spectra on the addition of alkali to a difference in the structure of the free *o*- and *p*-nitrophenols and *p*-nitrosophenols, as compared with the structure of the corresponding salts. The former are supposed to have the benzenoid configuration, whilst the quinonoid structure is ascribed to the salts.

H. M. D.

The Absorption Spectra of Phenoquinone, 2 : 5-Dianilino-*p*-benzoquinone, 2 : 5-Dianilino-*p*-benzoquinoneanil, and 2 : 5-Dianilino-*p*-benzoquinonedianil (Azophenine). D. S. PRATT and H. D. GIBBS (*Philippine J. Sci.*, 1913, **8**, 51—56).—A comparison has been made of the absorption spectra of phenoquinone, phenol, and *p*-benzoquinone. The absorption curves are quite distinct. In the case of phenoquinone, alcoholic solutions of 0·01 and 0·001 molar concentration give curves which are not continuous with the curve for a 0·1 molar solution or with each other. This is attributed to dissociation of the phenoquinone according to

$$C_6H_4O_2,2C_6H_5\cdot OH \rightleftharpoons C_6H_4O_2 + 2C_6H_5\cdot OH.$$

In support of this it is found that a solution prepared by dissolving *p*-benzoquinone and phenol in the requisite proportions has the same absorption curve as the solution prepared from phenoquinone. When phenol is used as solvent for the phenoquinone, the dissociation is a minimum, and the absorption curve which is obtained in these circumstances differs from that of *p*-benzoquinone to a much greater extent. Whereas *p*-benzoquinone shows a well-marked band, the curve for phenoquinone dissolved in phenol merely exhibits a step-off.

The other three compounds examined all show the quinone absorption band. The bands are well developed, and occupy much the same position. When phenol is employed as solvent instead of aniline or acetic acid, the dilution at which the band characteristic of the quinonoid structure makes its appearance is dependent on the nature of the adjacent groups. The band is observed with 0·1 molar solutions of *p*-benzoquinone, but a 0·001 or 0·0001 molar solution is sufficient in the case of dianilino-*p*-benzoquinone, dianilino-*p*-benzoquinoneanil, and azophenine. H. M. D.

The Cathodic Phosphorescence of Scheelites and Aluminas. CH. DE ROHDEN (*Ann. Chim.*, 1915, [ix], **3**, 338—366).—A more detailed account of work already published (compare A., 1914, ii, 694). W. G.

Radiometric Measurements of the Ionisation Constants of Indicators. II. M. G. PAULUS, J. F. HUTCHINSON, and HARRY C. JONES (*J. Amer. Chem. Soc.*, 1915, **37**, 1694—1704).—The radiometric method of determining the ionisation constants of indicators (Schaeffer, Paulus, and Jones, this vol., ii, 300) has now been applied to rosolic acid.

When a solution of rosolic acid, incompletely transformed by the addition of alkali, is left, the red colour becomes intensified, probably owing to a slow combination of the metallic phenoxide with the quinonoid complex. In solutions containing a large excess of alkali, a perceptible bleaching of the red colour takes place. The ratio of the red to the yellow component has been determined for indicator solutions of various hydrogen-ion concentrations. The values of the ionisation constant of rosolic acid, calculated from this ratio on the assumption that the indicator acid is monobasic, decrease as the alkalinity is reduced. When the hydrogen-ion concentration is increased from $2{\cdot}533 \times 10^{-8}$ to $19{\cdot}52 \times 10^{-8}$, the total salt concentration being $0{\cdot}0259N$, the value of the ionisation constant decreases from $5{\cdot}65 \times 10^{-8}$ to $2{\cdot}89 \times 10^{-8}$. This variation can be explained by regarding the indicator as a dibasic acid, and it is shown that the intensely coloured form of the indicator is produced when its first hydrogen is replaced by the base. E. G.

Rotatory Power. J. MINGUIN (*Ann. Chim.*, 1915, [ix], **3**, 367—394).—A résumé of work already published (compare A., 1903, i, 352, 428; 1905, i, 321, ii, 130; 1908, ii, 137; 1912, i, 237; 1914, ii, 403, 601). W. G.

The Connexion Between Natural and Magnetic Rotation Dispersion JOSEPH DAHLEN (*Zeitsch. wiss. Photochem.*, 1915, **14**, 315—342).—The question of the existence of a relation between the phenomena of natural and magnetic rotation dispersion has been examined by measurements of the rotatory power of optically isotropic crystals (sodium chlorate, bromate, and thioantimonate) and of optically uniaxial crystals belonging to the hexagonal system (strontium, lead, and potassium dithionate). The wave

length of the light used in the experiments extended from λ 671 to λ 436.

The results obtained show that the ratio of the natural to the magnetic rotation increases considerably with diminution of the wave-length in the case of the isotropic crystals, but that the variation is much smaller for the uniaxial crystals. The conclusion is drawn that the behaviour of optically isotropic crystals is not in agreement with Wiedemann's law (*Ann. Phys. Chem.*, 1851, **82**, 215), according to which the ratio of the natural and magnetic rotations is independent of the wave-length.

Some observations were also made with optically active liquids, including propyl *d*-tartrate, ethyl *d*-tartrate, *l*-menthone, *d*- and *l*-limonene, and *d*- and *l*-pinene. The results confirm those obtained by Darmois (A., 1911, ii, 352), and show that Wiedemann's supposed relation between the natural and magnetic rotation does not correspond with the facts. The relation in question is only applicable to particular substances, and quartz is one of these. H. M. D.

Experimental and Theoretical Investigations of Substances Showing Anomalous Dispersion of Molecular Rotatory Power. G. Bruhat (*Ann. Physique*, 1915, [ix], **3**, 417—489).—Continuing the study of anomalous dispersion and circular dichroism exhibited by active isotropic media having a selective absorption (this vol., ii, 302), the author has deduced from Drude's electromagnetic theory of the propagation of light in active absorbent media, Natanson's relation (A., 1910, ii, 170) between the signs of anomalous dispersion and circular dichroism, and also a simple relationship between the magnitude of these two phenomena. His results show that, between Drude's theory and the experimental results, there are not the contradictions as found by Ritz, but that the theoretical hypotheses as to the relative magnitudes of circular dichroism and anomalous rotatory dispersion, as well as to the anomalous refractive dispersion and its magnitude, are fully verified by the experimental measurements.

An examination of solutions of tartaric acid shows that the anomalous dispersion is not, in this case, accompanied by circular dichroism, and that it must therefore be explained on a chemical basis. The author considers that the results are to be explained by the existence of two active compounds in equilibrium, in proportions varying according to the nature of the solvent, the concentration, and the temperature. Measurements of the rotatory dispersion of tartaric acid in a pure, liquid, or superfused state show that the anomalies of dispersion are the same in the pure or the dissolved state, and that rise in temperature produced on the superfused acid the same effect as on solutions. The two compounds in equilibrium are therefore tartaric acid and a polymeride, the proportion of the latter being small. W. G.

The Action of Light on Chlorine Water. Alfred Benrath (*Zeitsch. wiss. Photochem.*, 1915, **14**, 238. Compare Benrath and Tuchel, A., 1914, ii, 447).—Polemical against Dawson (this vol., ii, 199). H. M. D.

Polychromism of Silver. R. Ed. Liesegang (*Zeitsch. wiss. Photochem.*, 1915, **14**, 343—346).—A discussion of the cause of the differences in colour which are exhibited by silver chloride gelatin films when acted on by suitable developing solutions. H. M. D.

Additive Products and the Photochemistry of the Hydrates of Chromic Chloride. V. V. Kurilov (*J. Russ. Phys. Chem. Soc*, 1915, **47**, 469—481. Compare A., 1914, ii, 404).—Additive products comprise substances formed by the union of whole molecules, and may possess either all or only some of the characteristics expressed in the laws of constant composition, valency and mass action, and in the phase rule. They are classified in five groups, the members of which: (1) are subject to all the fundamental characters of definite chemical compounds; (2) vary in composition with the concentrations of the reacting molecules, but obey the law of valency; (3) vary in composition, do not answer to the law of valency, but in solution or in the state of vapour give concentrations of the reacting molecules corresponding with the law of mass action; (4) show only unchanging composition, so that application of the phase rule is still possible; (5) change in composition in relation to time (compare A., 1911, ii, 873; Kurnakov, Shemtschushni, and Tararin, A., 1913, ii, 410).

Various examples are given, showing that the reactions of magnesium, zinc, and copper salts with excess of ammonia solution represent processes of formation of additive products of class (5), micellæ or granules, and not molecules, being emitted into the solution; for example, on addition of ammonia solution to zinc chloride, in the region of increasing precipitate, the additive product, $ZnCl_2,3Zn(OH)_2$, belonging to class (1) is formed at the bottom of the vessel. Solution in excess of the reagent takes place simultaneously with transformation of the above additive product into a more complex form, $ZnCl_2,mZn(OH)_2$, the magnitude of m varying with the concentration, and the law of mass action hence becoming inapplicable; this compound belongs, therefore, to class (5).

The results previously obtained are discussed (compare A., 1906, ii, 343, 349; 1908, ii, 477; 1914, ii, 404). T. H. P.

Photochemical Reactions of Compounds of Rare Elements. Alfred Benrath (*Zeitsch. wiss. Photochem*, 1915, **14**, 217—222).—Photochemical reactions are described, in which compounds of thallium, cerium, titanium, tellurium, selenium, sulphur, and iridium are involved.

The thallous haloids are reduced to metal in presence of reducing agents, such as oxalic, tartaric, and citric acid and the alcohols. The reaction velocity diminishes rapidly in the series chloride, bromide, iodide. Thallous sulphate appears to be quite stable in similar circumstances. In presence of sulphuric acid the oxidation of oxalic acid is a catalytic reaction represented by $H_2C_2O_4 + 2TlCl = 2Tl + 2HCl + 2CO_2$, $2Tl + H_2SO_4 = Tl_2SO_4 + H_2$, $Tl_2SO_4 + 2HCl = 2TlCl + H_2SO_4$.

Thallic salts react even more readily with reducing agents in

presence of light. The products of the reaction depend on the nature of the incident light rays, on the reducing agent, and on the period of insolation. By varying the conditions of the experiment, thallic bromide was found to yield the dibromide, $TlBr_2$ (yellow needles), the sesquibromide, Tl_2Br_3 (red needles), thallous bromide, and metallic thallium.

The activity of ceric salts as oxidising agents is greatly increased by the action of light. It has been found that the fatty acids and benzoic acid are oxidised by ceric sulphate in aqueous solution. Acetic acid yields formaldehyde, and propionic acid gives acetaldehyde.

Titanic compounds are reduced to the corresponding titanous compounds by alcohols, oxalic and oxy-acids. Telluric and tellurous acid are reduced to tellurium, selenic and selenious acid to selenium, and sulphurous acid to sulphur in similar circumstances.

Iridium compounds are reduced in stages, with the ultimate formation of metallic iridium. H. M. D.

Theory of the Becquerel Effect. Electrical Methods of Photochemistry. A. GOLDMANN (*Zeitsch. Elektrochem.*, 1915, **21**, 73—80).—The author has examined the Becquerel effect by measuring the current produced and the *E.M.F.* of electrodes of copper foil, both in the dark and in bright light. Various solutions were used as electrolyte in the measurements, which included 0·2*N*-sodium sulphate, 0·2*N*-calcium chloride, 0·05—1*N*-sodium chloride, and various solutions of sodium bromide, strontium chloride, barium nitrate, and lithium sulphate. It is shown that the photoelectric current increases almost linearly as the potential of the electrode sinks from +0·4 volt to +0·1 volt, after which the curve bends. In the region where the potential approaches the zero value the photoelectric current reaches a limiting value, which on further decreasing the potential remains constant. The photoelectric current is uninfluenced by the ions from neutral solutions of chlorides, bromides, sulphates, and nitrates of the alkalis and alkaline earths. On changing the solvent of the electrolyte from water to methyl alcohol there is no appreciable change in the photoelectric current; consequently in general it follows that a change in the electrolyte, the concentration of the electrolyte, and the solvent produces no change in the photoelectric current. From this it follows that the photoelectric current is not produced by the mutual action of the electrode and the solution, but by a direct action of the light on the oxide layer. Since the effect is the same when electrodes with different thicknesses of oxide are used, it follows that the current must arise at the surface of the oxide layer. Since the photoelectric current remains constant during a prolonged action of light, it follows that a definite number of electrons must be expelled per unit of time. On increasing the electrode potential the photoelectric current is weakened, and since the increased potential of the electrode works against the discharge of electrons it follows that the decrease in the photoelectric current is to be attributed to an opposing current of electrons to the

electrode. The photoelectric current increases proportionally with the intensity of illumination of the electrode; consequently the number of electrons expelled per unit of time is proportional to the light intensity. With regard to the potential of the electrode, it is shown that there is a direct relationship between the original potential of the electrode and the amount of change produced by illumination. In the case of potential measurement with a constant current flowing, it is shown that the relationship between the original potential and the change on illumination is almost linear. It is shown that the dependence of the potential change on the composition of the electrolyte solution observed by Rigollot is due, in the first place, to a shift of the initial potential of the electrode, and the negative temperature-coefficient of the potential change is due to the overwhelming temperature-coefficient of depolarisation. J. F. S.

A Method of Calculating the Absorption Coefficients of Different Substances for Homogeneous *X*-Radiation. H. Moore (*Proc. Physical Soc., London*, 1915, **27**, 432—438. Compare A., 1914, ii, 88; this vol., ii, 401).—It has been shown in a previous paper (*loc. cit.*) that the number of electrons emitted by an atom subjected to *X*-radiation is proportional to the fourth power of its atomic weight (or possibly its atomic number). The coefficients of absorption of different elements for the same type of *X*-radiation are also proportional to the fourth powers of the atomic weights. The number of electrons liberated by a monatomic element in vapour form at a pressure of 760 mm. is given by the expression $1{\cdot}05 \times 10^5 \times A^4$, where A is the atomic weight, if the corpuscular radiation emitted by air is taken as unity. This expression will also afford the relation between the absorption coefficients.

By means of the density law, the constant in the above expression may be applied in the calculation of the absorption-coefficients of the solid metals, and by assuming an additive law for compounds, the absorption-coefficients of these may be calculated. The agreement between the calculated and observed values is quite close over a considerable range of radiations and absorbers. If, however, the atomic weight of the absorber is greater than that of the radiator, in which case the K series is absent from the secondary radiation excited in the absorber, the calculated and observed values are no longer in agreement. It is suggested that this discontinuity is associated with selective absorption. H. M. D.

Occurrence of Radioactive Waters in Norway. E. Poulsson (*Chem. Zentr.*, 1914, ii, 1469).—Examination of 100 different waters of Norway showed that almost all the waters were radioactive, although in most cases the activity was slight. The more active waters were obtained from springs at Vessetrud, Näsodden, and Jellum, and from wells at the Tandberggehöft, Simoatal. W. P. S.

The Radioactivity of Minerals. I. Pyromorphite M. Bamberger and G. Weissenberger (*Monatsh.*, 1915, **36**, 169—174).—An examination of the radium and thorium contents of pyromor-

phite from various sources by radioactive methods showed that whereas the radium content varied considerably for different specimens, from $1{\cdot}3 \times 10^{-9}$ to 3×10^{-13} gram of radium per gram, the thorium content was more constant, from $1{\cdot}2 \times 10^{-4}$ to $1{\cdot}3 \times 10^{-5}$ gram of thorium per gram. The mineral was shown to be homogeneous as regards its radium content, by dissolving the superficial layers of a crystal, and comparing the radium contents of the dissolved and undissolved portions, no difference between them being found. Danne's view that a surface concentration of radium on the mineral had occurred from percolating water containing radium is not tenable. Spring waters flowing through radioactive minerals dissolve almost alone the radium and mesothorium, leaving the uranium and thorium. Pyromorphite is regarded as a young formation, in which the radium deposited at the time of formation from the water in which the mineral was formed has not completely decayed, whereas the mesothorium deposited at the same time has completely decayed, leaving only the minute quantity of thorium deposited with the mineral. This accounts for the great variation in radium content and comparative constancy of the thorium content. F. S.

Problems of Complex Molecules. P. Lenard (*Chem. Zentr.*, 1915, i, 930 ; *Sitzungsber. Heidelberg. Akad. Wiss.*, 1914, 27, 28, 29).—I. *Evaporation and Osmotic Pressure.*—Since the charge on an electrically charged liquid does not evaporate with the liquid, the charged molecules, which form complexes of high molecular weight, do not evaporate at all, being on account of their complex nature drawn back into the liquid by stronger molecular forces than the ordinary molecules. The presence of such molecules causes a reduction of the vapour pressure, and the existence of complex molecules of the solute and the solvent on the surface of solutions is the underlying cause of the vapour pressure law and the laws of osmotic pressure.

II. *Molecular Forces and their Electric Action; Waterfall Electricity.*—The forces which act on the complex molecules on the surface can be expressed as a function of the volumes of the molecules, the mass of their spheres of action, and the temperature, and can be approximately calculated in absolute units. Observations on waterfall electricity furnish experimental data. The surface layer consists here of an electric double layer the moment of which is connected with the dielectric constant of the liquid. The author deduces that in general the molecular force is proportional to the product of the density and the dielectric constant of the substance less 1, and since $D-1$ is proportional to the electric moment of unit volume the electric nature of the molecular force follows. In place of the unmeasurable molecular force, surface tension may be substituted.

III. *Character of the Surface of Liquids; Seat of the Electrostatic Charge; Condensation of Vapour.*—The usual conception that the electric charge is distributed on the outermost superficial layer is replaced by a more refined idea which takes account of

molecular structure. Electric and non-electric fog nuclei do not show so great a difference, in respect to the condensation of vapour, as is usually supposed. G. F. M.

Method for Ascertaining the Geometrical Asymmetry of Molecules. THE. SVEDBERG (*Jahrb. Radioaktiv. El-ktronik.*, 1915, **12**, 129—146).—In a previous paper (A., 1914, ii, 97) it has been shown that the electrical conductivity of anisaldazine changes when it is placed under the influence of a magnetic field, and that the change in question varies according to whether the conductivity is measured along or across the lines of magnetic force. The phenomenon has now been further examined in experiments with a number of crystalline liquids, in which electrolytes, inorganic and organic, were dissolved. The influence of the strength of the field, of the period of its application, and also of temperature on the phenomenon, has been described elsewhere.

The ratio of the conductivity along the lines of force κ_0 to that across the lines κ_{90} is taken as a measure of the anisotropic conductivity effect. For two different electrolytes in the same crystalline liquid solvent it is found that the ratio of the κ_0/κ_{90} values is independent of the temperature. For a given pair of electrolytes this ratio is also independent of the nature of the solvent. Since it is also independent of the strength of the magnetic field (if sufficiently great) it seems permissible to regard the ratios κ_0/κ_{90} as affording a measure of quantities which are characteristic of the electrolytes.

From observations made with a number of electrolytes dissolved in *p*-azoxyphenetole, it is found that the ratio κ_0/κ_{90} varies with the nature of the electrolyte. At 10° below the clearing temperature, the following values were obtained: hydrogen chloride, 1·284; hydrogen bromide, 1·285; hydrogen iodide, 1·283; nitric acid, 1·450; quinol, 1·43; catechol, 1·46; pyrogallol, 1·44; *m*-nitrophenol, 1·44; picric acid, 1·42; trinitroresorcinol, 1·45; β-naphthol, 1·583; 3-hydroxy-β-naphthoic acid, 1·587; lithium dinitro-α-naphthoxide, 1·591. According to these numbers, the six derivatives of benzene give very nearly the same value of κ_0/κ_{90}, which is considerably greater than the value afforded by the halogen acids, and less than the value exhibited by the naphthalene derivatives. With one exception, these substances are acids, and since the positive ion is the same in the different solutions, the observed differences in κ_0/κ_{90} are to be attributed to the anions. It is supposed that the differences afford evidence of differences in the geometrical configuration of the anions. The value of the ratio κ_0/κ_{90} for any ion expressed in terms of the ratio for the halogen ions is considered to afford a measure of the geometrical asymmetry. According to this, the degree of asymmetry of all the benzene derivatives examined is the same, and is much less than that of the naphthalene derivatives. H. M. D.

Electro-chemistry of Non-aqueous Solutions. XIII. Ionisation of Bromine Solutions of Iodine Trichloride. V. A. PLOTNIKOV and V. E. ROKOTJAN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 723—730).—It has been shown previously (A., 1913, ii, 378) that

bromine solutions of iodine exhibit moderately high electrical conductivity, which is regarded as due to the ionisation of the iodine bromide formed in the solution. Experiments have now been carried out at 25° with solutions of iodine trichloride in bromine and in dichloroacetic acid, those in carbon tetrachloride, silicon tetrachloride, and chloroform being non-conducting.

Solutions of iodine trichloride in bromine exhibit no appreciable conductivity until the concentration reaches a value of about 18%, the specific conductivity then rising rapidly from 7·3 to 214×10^{-6} reciprocal ohms for a concentration of 31·4%. The molecular conductivity is enormously greater than that of iodine bromide, and diminishes rapidly with increase of the dilution, this variation being of the so-called "anomalous" type. As has been shown already (A., 1902, ii, 639), such diminution of the molecular conductivity with the concentration may be explained by the decomposition of complex ions. Assuming that iodine trichloride is a binary electrolyte, its electrolytic dissociation would be expressed by the equation $ICl_3 \rightleftarrows I^+ + [Cl_3]^-$; on dilution of the solution the complex anion would then undergo decomposition into a molecule of chlorine and an ordinary chlorine ion, which would combine with the iodine cation to form a neutral molecule of iodine chloride. Investigation of the electrolysis of iodine trichloride dissolved in bromine or in dichloroacetic acid indicates that the chlorine forms ions of two kinds, namely, Cl^- and Cl_3^-, the latter constituting at least 59% of the mixture. T. H. P.

Certain Electrochemical Properties of Solutions. A. Bogorodski (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 379—393).—The author applies his views on hydrolytic dissociation (compare this vol., ii, 418; also Sachanov, this vol., ii, 526) to the explanation of various electrochemical phenomena of solutions, for example, the lower values almost always given for i by measurements of the electrical conductivity of salt solutions in comparison with those obtained from thermochemical data, the electromotive forces of voltaic and concentration cells, etc. He does not regard the heats of neutralisation of lithium, sodium, and potassium hydroxides by one and the same acid as being identical, as Thomsen stated, but as only approximately equal. T. H. P.

Electromotive Forces in Alcohol. VI. Absolute Potentials by the Capillary Electrometer. Edgar Newbery (T., 1915, **107**, 852—857. Compare T., 1914, **105**, 2553).—By measuring the *E.M.F.* which must be applied to mercury in various aqueous and alcoholic solutions to produce the maximum surface tension the author has determined the potential of mercury in those solutions. The following values are obtained at 20°: saturated aqueous solution of sodium chloride, 0·481 volt; normal aqueous solution of sodium chloride, 0·531 volt; decinormal aqueous solution of sodium chloride, 0·580 volt; saturated alcoholic solution of sodium chloride, 0·481 volt; saturated solution of ammonium chloride in water, 0·420 volt; and saturated solution of ammonium chloride

in alcohol, 0·423 volt. The figures observed for the saturated solutions seem to confirm the view of Lapworth that the potential of a metal in a saturated solution is the same whether the solvent be water or some other solvent, provided that each ion involved has the same affinity for water as for the other solvent. The temperature-coefficient of N and $N/10$-aqueous solutions of sodium chloride are found to be +0·0006 and +0·0008 volt per degree respectively. J. F. S.

Potential of Silver against Silver Ion in Concentrated Solutions of Potassium and of Sodium Chloride, and its Relation to the Activities of Such Solutions. GEORGE SHANNON FORBES and FREDERICK OSBAND ANDEREGG (*J. Amer. Chem. Soc.*, 1915, **37**, 1676—1685).—Many measurements have been recorded of the potential of silver electrodes against dilute chloride solutions, saturated with silver chloride, but attempts do not seem to have been made hitherto either to carry out such determinations with concentrated solutions or to investigate solutions not saturated with silver chloride.

Potential measurements have now been made, using silver electrodes, concentrated solutions of sodium and potassium chlorides saturated with silver chloride, and a junction of concentrated potassium nitrate to eliminate diffusion potentials, and from the results the activity of the chloride ion in the concentrated solutions has been calculated. The solubility product is assumed to be constant, and evidence is adduced showing that its variations do not greatly affect the results. The values obtained by this method are always lower than those calculated from conductivities, except in the most concentrated solutions of sodium chloride. The dissociation, calculated from these values, reaches a minimum at 1·7N. Solutions variable in alkali chloride but constant in silver chloride give results supporting the view that the complex K_3AgCl_4 exists in concentrations above 1·7N. E. G.

Potassium Chloride Concentration Cells. DUNCAN A. MACINNES and KARR PARKER (*J. Amer. Chem. Soc.*, 1915, **37**, 1445—1461).—This work was undertaken with the objects of measuring the free energy of dilution of potassium chloride by the *E.M.F.* method and of investigating liquid junctions connecting salt solutions of different concentrations (C_1 and C_2) by comparing the *E.M.F.*'s of cells in which these junctions are present with similar measurements on cells so constructed as not to make this somewhat troublesome point of contact.

The *E.M.F.*'s of "concentration cells without transference" of the form:

$$Ag\,|\,AgCl,KCl(C_1)\,|\,K(Hg)_x - K(Hg)_x\,|\,KCl(C_2),AgCl\,|\,Ag$$

have been determined and compared with measurements of the *E.M.F.* of "concentration cells with transference" of the form $Ag\,|\,AgCl,KCl(C_1)\,|\,KCl(C_2),AgCl\,|\,Ag$. It is shown that when the same solutions are used in cells of both types the ratio of the potentials gives accurate values of the transference number of the cation.

The results indicate that the "activities" of the ions (Lewis, A., 1908, ii, 16) from potassium chloride are much lower than the concentrations as calculated from conductivity determinations. The values of the "activity" and of the concentration, however, seem to approach the same limit for very dilute solutions. E. G.

Electrolytic Deposition of Alloys and the Metallographical and Mechanical Investigation. VI. The Pyrophoric Cathodic Deposits from Mixed Solutions of Iron Sulphate and Magnesium Chloride Containing Glycerol. Robert Kremann and Josef Lorber (*Monatsh.*, 1914, **35**, 1387—1422. Compare A., 1914, ii, 96, 422, 615, 616).—A number of experiments are described on the electrolysis of mixed solutions of iron sulphate and magnesium chloride in 75% glycerol water mixtures. The electrolyses were effected between iron anodes and cathodes of copper or of iron covered with graphite, and without diaphragms. The current density was constant throughout the series, and had a value 0·26 amp./dcm.^{2}. The ratio of the two salts varied between the limits $FeSO_4,7H_2O : MgCl_2,6H_2O = 0·55 - 1·79$. It is shown that with the ratio 0·55 a deposit consisting of 34·20% Fe, 8·45% Mg, 5·26% C, and 1·98% H is obtained. This deposit can scarcely be termed metallic, and consists in all probability of a mixture of oxides of iron and magnesium, and a carbon compound rich in oxygen. As the ratio increases the percentage of iron in the deposit increases very rapidly at first, and then more slowly; both the magnesium and carbon decrease in the deposit. As the ratio of the two salts is increased from 0·76 the deposit becomes more and more pyrophoric up to the ratio 1·25, when the pyrophoric character begins to diminish, and has entirely disappeared at the ratio 1·70. It is shown that the magnesium has little to do with the pyrophoric character of the alloy, but that a definite percentage of carbon is necessary. The pyrophoric character is determined by scratching the deposit with steel, when sparks are produced. Further experiments were carried out in a 50% glycerol water solution of the same salts. The ratio of the two salts in these experiments was 0·55, 1·00, and 1·79; the current densities used were 0·26, 0·52, and 1·31 amp./dcm.^{2}. It is shown that the iron content of the deposit passes through a maximum at the ratio

$$FeSO_4,7H_2O : MgCl_2,6H_2O = 1,$$

and at the same ratio with current densities of 0·52 and 1·31 the carbon content passes through a minimum, whereas at the current density 0·26 the carbon content rapidly increases and then remains constant with increasing ratio of the two salts. The magnesium content is practically constant (0·4—0·5%), except in the case of current densities 0·52 and 1·31 at the ratio

$$FeSO_4,7H_2O : MgCl_2,6H_2O = 1,$$

when it almost vanishes. The alloys deposited have a decided metallic appearance, and are not pyrophoric. Experiments are next made with 25, 60, and 80% glycerol solutions; it is shown that the deposit becomes less metallic with increasing concentration of glycerol, and the percentage of magnesium and carbon in the

deposit increases as the glycerol content increases. Temperature affects the deposit to a marked degree; in cases where the product is not pyrophoric when deposited at ordinary temperatures, it becomes so when deposited at 60°. Pyrophoric deposits have been obtained in the absence of magnesium chloride in the solution, thus proving that the magnesium in the deposit has nothing to do with the pyrophoric character of the alloy. Further experiments are described on the microscopic structure of the deposits, of which a number of photographs are given. The hardness and the electromotive behaviour of the alloys are investigated. In the latter case the *E.M.F.* is measured of cells made up thus: Deposit|*N*-$FeSO_4$ solution|Normal Electrode and Deposit|*N*-$MgSO_4$ solution|Normal Electrode. These results show that the potential obtained as soon as the alloy is dipped into the solution is abnormally high, but becomes normal after some time. J. F. S.

"Mobilisation" of Metals. M. Centnerszwer (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 537—539).—Polemical against Thiel (this vol., ii, 218). T. H. P.

Emissivity of Metals and Oxides. IV. Iron Oxide. George K. Burgess and Paul D. Foote (*J. Washington Acad. Sci.*, 1915, **5**, 377—378. Compare this vol., ii, 42).—The total and monochromatic emissivity of the oxide formed by heating iron in air has been determined. The emissivity for radiation of wave-length $\lambda = 0{\cdot}65\ \mu$ varies from 0·98 to 0·92 over the interval 800—1200°. The corrections to be applied to the readings of an optical pyrometer over this range vary from 0° to 10°. The total emissivity of the oxide increases from 0·85 at 500° to 0·89 at 1200°, and the pyrometer corrections vary from 30° to 50°. H. M. D.

Depression of the Freezing Point. V. A. Vilde and A. J. Bogorodski (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 373—379).—The authors discuss the explanations which have been advanced of the abnormal depressions of freezing point produced by various solutes. More or less concordant data obtained by different investigators show that liquid water is polymerised, the polymerisation index being either 2 or 3. On the basis of the oxonium and hydronium theories (compare Hantzsch, A., 1908, ii, 14; 1909, ii, 18, 973), it is possible to represent liquid water as "trioxylene," $H_2O<\begin{matrix}OH_2\\|\\OH_2\end{matrix}$, such a structure being supported by the absence of electrical conductivity. The presence of an acid, HR, or a base, M·OH, would then give rise to the following reaction, resulting in the formation of the doubled number of molecules:

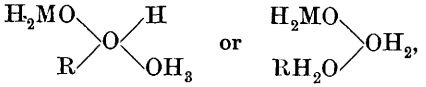
$$(H_2O)_3 + HR = H_3O{\cdot}R + H_3O{\cdot}OH$$

or $(H_2O)_3 + M{\cdot}OH = H_2MO{\cdot}OH + H_3O{\cdot}OH$. With a salt, the reaction would be expressed thus:

$$(H_2O)_3 + MR = H_3O{\cdot}R + H_2MO{\cdot}OH,$$

and in concentrated solutions the chemical forces between

$H_2MO{\cdot}OH$ and $H_3O{\cdot}R$ would lead to the formation of undissociated molecules,



which would explain the ready decomposition of the saturated solution into the anhydrous salt, MR, and $(H_2O)_3$.

Cryoscopic investigation of two dilute solutions of cupric oxide in anhydrous acetic acid gave the mean value, $i=1{\cdot}37$, and the conclusion is drawn that the phenomenon of the depression of the freezing point of the acetic acid by the oxide is identical with that observed with water and an anhydrous salt. In the latter case, therefore, the explanation may be that the number of molecules is increased owing to the formation of new molecules by the reaction between solute and solvent. Analogous cases are those in which the solidifying point of alkali hydroxide is lowered by the action of various salts and oxides, for instance,

$$n\mathrm{KOH}+\mathrm{PbO}=\mathrm{Pb(OK)_2}+\mathrm{H_2O}+(n-2)\mathrm{KOH}.$$

In dilute solutions, thiocarbonates, which react with water according to the equation $K_2CS_3+3H_2O=K_2CO_3+3H_2S$, may give a value for i greater than 4. Further experiments are being made.

T. H. P.

The General Theory of Corresponding States and the Thermodynamic State Equation. George von Kaufmann (*Phil. Mag.*, 1915, [vi], **30**, 146—162).—The theory of corresponding states is analysed, and a new method of obtaining the reduced equation of condition is described. Emphasis is laid on the fact that the theory of corresponding states is in its foundations independent of the existence of the critical phenomena. By assigning to every substance special or specific units of p, v, and T, three specific constants are eliminated from the equation of state. The usual method is to put $p_k=v_k=T_k=1$ for each substance, where k has reference to some arbitrarily selected critical point. A more fundamental and general method of choosing specific units is described, and it is shown that this method, when applied to the van der Waals' equation, leads to the "algebraic" reduced equation $(\pi+1/\phi^2)(\phi-1)=\theta$. This purely algebraic method is essentially similar to the usual method, and affords a direct expression of the theory of corresponding states.

It is shown that the method may be applied to phenomena involving other than the purely thermodynamic quantities p, v, and T.

In the second part of the paper the question of the equations connecting temperature, pressure, and co existing volumes in liquid-vapour systems is discussed, and the author shows how the complete conditions of equilibrium may be calculated from the equations of state of van der Waals, Berthelot, and Clausius. H. M. D.

Relation Between Boiling Point and Constitution. L. Casale (*Gazzetta*, 1915, **45**, i, 567—579, and *Atti R. Accad. Sci. Torino*, 1915, **50**, 809—822).—The formulæ suggested by Walker (T., 1894,

65, 193), Ramage (A., 1904, ii, 467), Boggio-Lera (A., 1899, i, 843), and Sugden (A., 1914, ii, 799) for expressing the boiling point of a compound as a function solely of the molecular weight furnish no more satisfactory conclusions of this problem than Kopp's original attempt, since they are incompatible with the phenomenon of isomerism. Young's formula (A., 1905, ii, 231), although based on different principles, is valid only for the normal paraffins, and does not correspond with the requirements of isomerism, and the author proposes its replacement by the expression $\Delta = 109{\cdot}2/n^a$, which gives the rise in boiling point due to the substitution of a hydrogen atom by a methyl group in terms of the absolute boiling point of methane, 109·2°, and the number, n, of carbon atoms; a is an arbitrary constant.

Ramage held that the lower members of the saturated hydrocarbons should not be regarded as true homologues, and Young subsequently separated the homologous series into two groups; in the case of the paraffins, propane forms the last term of the first group and the first term of the second group. These considerations are developed by the author in the following manner: The compounds, CH_4, $CH_3{\cdot}CH_3$, $CH_2(CH_3)_2$, $CH(CH_3)_3$, $C(CH_3)_4$, form a continuous series, passage from one term to the next being effected by introduction of a methyl group in place of a hydrogen atom of methane. In the series $CH_3{\cdot}CH_2{\cdot}CH_3$, $CH_3{\cdot}[CH_2]_2{\cdot}CH_3$, $CH_3{\cdot}[CH_2]_3{\cdot}CH_3$, etc., the first term is one, but not the last, term of the first series. It may be supposed that the rise of boiling point occurring in the passage from one member to the next higher homologue is proportional to the force with which the added group is attracted to the carbon atom or atoms to which it is linked. This force will remain almost constant throughout the second series, but will vary continuously in the first series, commencing with ethane, the substituent methyl groups uniting successively with $\cdot CH_3$, $\cdot CH_2\cdot$, $>CH\cdot$, and $>C<$. In the formula now proposed by the author, the values of a will be proportional to the forces in these four cases, the calculated numbers being 0·61, 0·675, 0·74, and 0·805 respectively. The value 0·675, calculated for propane in the first series, will hold for all terms of the second series, so that the boiling point of any member, C_nH_{2n+2}, of this series will be given immediately by $\Sigma(109{\cdot}2/n^{0{\cdot}675})$. For a member of the first series, however, for instance, $\beta\beta$-dimethylpropane, the boiling point will be given by the formula $\Sigma(109{\cdot}2/n^{0{\cdot}805})$, n having here the value 5. With a saturated hydrocarbon belonging to both series, for example, $CH_2Me{\cdot}CH_2{\cdot}CHMe_2$, the boiling point is calculated with reference to that of the fundamental hydrocarbon, which is here butane; thus the boiling point will be given by: $109{\cdot}2/1^{0{\cdot}675} + 109{\cdot}2/2^{0{\cdot}675} + 109{\cdot}2/3^{0{\cdot}675} + 109{\cdot}2/4^{0{\cdot}675} + 109{\cdot}2/5^{0{\cdot}74} + 109{\cdot}2/6^{0{\cdot}74}$, the sum of the first four terms giving the boiling point of butane, and the sum of the last two the rise due to the two methyl groups connected with one $:CH\cdot$ group. This method of calculation gives values mostly in good but varying agreement with the experimental boiling points of the normal saturated hydrocarbons. In the case of nonadecane, however, the calculated value is 606·7° and the

observed 603·0°. The author considers the accuracy of the latter open to doubt, in view of the high temperature and also of the fact that the values of the ratio $T_{760} : T_{15}$ for the C_{15}, C_{16}, C_{17}, C_{18}, and C_{19} terms of the series are 1·3003, 1·3020, 1·3002, 1·2982, and 1·2940 respectively; multiplication of the values of T_{15} for $C_{18}H_{38}$ and $C_{19}H_{40}$ by 1·3 gives 591° and 606°, the author's calculated values being 591·75° and 606·7°.

Similar good agreement is obtained with the saturated hydrocarbons containing branched chains, the mean error being 0·75°. An analogous method of calculation gives the absolute boiling points of ethylenic hydrocarbons. The boiling point of ethylene itself being 170·5°, that of $CH_2{:}CHMe$ will be $170·5 + 109·2/3^{0·615}$, 0·615 being the value of a for a methyl group attached to the ·CH: residue. In the case, however, where both hydrogen atoms of one of the methylene groups of ethylene are replaced, a will have the value 0·675 (*vide supra*); thus, $CH_2{:}CMe_2$ will have the boiling point $170·5 + 109·2/3^{0·675} + 109·2/4^{0·675}$. With the ethylenic hydrocarbons, the agreement between the observed and calculated boiling points is not so good as with the saturated hydrocarbons, the mean divergence being 1·6°.

The values found by different investigators for the boiling points of the normal, saturated hydrocarbons are in fairly good agreement for the second and succeeding members of the series, but greater differences occur with methane, the mean of the values obtained by Wroblewski, Olszewski, and Ladenburg and Krügel being 114·3°. An attempt is made to overcome this difficulty in the following manner. The boiling point of a normal, saturated hydrocarbon is a function of the number of carbon atoms in its molecule, and in the case of isomerides the boiling point is usually lowered by increase in the number of methyl groups in the molecule. It is easy to show that, in the substitution of a hydrogen atom by a methyl group, the presence of other methyl groups united to the same carbon atom lowers the increase of boiling point produced. Quite generally, then, the boiling point of a saturated hydrocarbon, C_nH_{2n+2}, may be regarded as a sum to which the central groups, CH_2, CH, and C, contribute always the same amounts, whilst the terminal methyl groups contribute different amounts according as one or more are combined with the same carbon atom. If a represents the number of central groups, b the number of isolated methyl groups, and c, d, and e respectively the numbers of methyl groups united in pairs, threes and fours to single carbon atoms, the absolute boiling point is given by: $T = 114/1^{0·7} + 114/a^{0·7} + 114/(a+1)^{0·77} + 114/(a+2)^{0·77} + \ldots + 114/(a+b)^{0·77} + 114/(a+b+1)^{0·8033} + 114/(a+b+2)^{0·8033} + \ldots\ldots + 114/(a+b+c)^{0·8033} + 114/(a+b+c+1)^{0·8366} + \ldots + 114/(n-e)^{0·8366} + 114/(n-e+1)^{0·87} + 114/(n-e+2)^{0·87} + \ldots + 114/n^{0·87}$. In the case of the normal paraffin this sum assumes the form:

$$T = \overset{(n-2)}{\Sigma} 114/(n-2)^{0·7} + 114/(n-1)^{0·77} + 114/n^{0·77}.$$

Application of this formula to the normal, saturated hydrocarbons gives values showing mean differences of 0·60° and 1·18° from the

observed boiling points at 760 mm. and 15 mm. respectively; to obtain the values at a pressure of 15 mm., the value 114/1·3 is substituted in the formula for 114. With the saturated hydrocarbons containing branched chains, this mean difference at 760 mm. is 0·71°. T. H. P.

Heat of Vaporisation and Molecular Association in Liquids. M. M. GARVER (*J. Physical Chem.*, 1915, **19**, 500—512).—Polemical An answer to Tyrer's criticism (this vol., ii, 87) on the conclusions put forward previously by the author (A., 1912, ii, 830; 1913, ii, 24). J. F. S.

The Vapour Pressure of Liquids in the Presence of Gases. F. H. CAMPBELL (*Trans. Faraday Soc.*, 1915, **10**, 197—206).—The liquid to be examined is saturated with hydrogen and introduced into a narrow tube, which can be sealed at both ends. The sealed tube is then pushed through a rubber stopper and deeply scratched at a point slightly above the level of the rubber. The stopper is pushed into the lower end of the measuring vessel, which is connected with a manometer and filled with hydrogen. A layer of mercury prevents leakage at the stopper. The measuring apparatus being immersed in a thermostat, it is filled with hydrogen, and brought into equilibrium, and the reading of the manometer is then taken. The tube containing the liquid is then broken at the scratch, the liquid is displaced by mercury, and the apparatus is thoroughly shaken to ensure saturation. The vapour pressure is now given by the difference between the initial and final readings of the manometer. The apparatus is of very simple construction.

The values obtained for the vapour pressures of a number of liquids are in good agreement with the accepted values, but are slightly lower. A review of previous investigations shows that the vapour pressure of a liquid in contact with a gas is always lower than when in contact with its own vapour only. The most important results are those of Regnault (*Ann. phys. chim.*, 1845, [iii], **15**, 129; *Mém. Acad. Sci.*, 1862, **26**, 679). The lowering of vapour pressure of any liquid increases with the solubility of the gas, but the lowering is always greater than can be accounted for by the quantity of gas dissolved. Violent agitation of the liquid tends to obliterate the differences. It is suggested that the concentration of gas is greater in the surface layer than in the body of the liquid. C. H. D.

Physical Constants of Alcoholic Liquids. E. BARBET (*Bull. Assoc. Chim. Sucr. Dist.*, 1914, **32**, 43—49).—A table is given showing the specific gravity, boiling point, specific heat, and latent heat of mixtures of water and alcohol, and of the distillates yielded by the mixtures boiling at a constant temperature. Results recorded previously for the specific heat and latent heat of the mixtures are criticised as having been deduced from insufficient data. W. P. S.

Fractional Distillation. CH. MARILLER (*Bull. Assoc. Chim. Sucr. Dist.*, 1914, **32**, 99—104).—The physical properties of binary mixtures

such as water and alcohol, alcohol and carbon disulphide, etc., afford a means of estimating the constituents of the liquids, and may be applied for ascertaining the composition of distillates obtained in fractional distillation. The specific gravity, refractive index, viscosity, and, in certain cases, the boiling point, give the most useful data. The author also discusses the analysis of ternary mixtures. W. P. S.

Preparation of Anhydrous Solids. William Ringrose Gelston Atkins and (Miss) Edith Gertrude Wilson (T., 1915, **107**, 916—918).—It is shown that lævulose, maltose, and starch can be completely dehydrated by adding to a quantity of the slightly moist substance a mixture of dry alcohol and benzene. The mixture is distilled, using a Young and Thomas fractionating column of eight sections. A ternary mixture of water, benzene, and alcohol is first removed; when all the water has been removed, the distillate becomes clear, and the temperature rises to 68·25°, the b. p. of the binary constant-boiling mixture of alcohol and benzene, and remains there until the whole of one of the constituents has distilled. The residue of the other constituent is then removed, under reduced pressure if necessary, and the solid dried by gentle heating.

J. F. S.

Heat of Formation and Polymerisation of Some Oxides and Determination of the Heat of Combination of Water by Fusion with Sodium Peroxide. W. G. Mixter (*Amer. J. Sci.*, 1915, [iv], **40**, 23—32).—The heat of formation of magnesium oxide, ferric oxide, titanium dioxide, silica, and zinc oxide has been determined by fusing the hydrated oxide with sodium peroxide and either sulphur or carbon in a calorimetric bomb. The reaction occurring in the case of magnesium oxide is represented:

$$S + 3Na_2O_2 + MgO,H_2O = Na_2SO_4 + MgO + 2NaOH + Na_2O.$$

Calculating from known values, the heats of hydration, formation, and polymerisation of the oxides mentioned are deduced.

J. F. S.

Temperature of Decomposition of Copper Nitrate. Luigi Rolla (*Gazzetta*, 1915, **45**, i, 444—450).—The object of the experiments here described was to determine experimentally, and to calculate from thermochemical data, the temperature at which the reaction, $2CuO + 4NO_2 + O_2 = 2Cu(NO_3)_2$, takes place under the ordinary atmospheric pressure. The mixed gases, obtained by heating lead nitrate, were passed for two hours over a weighed quantity of dry copper oxide maintained at a constant temperature in an electric resistance furnace, the change in weight of the oxide being measured. It is found that, at 250°, nitrogen peroxide and oxygen at a pressure of 1 atmosphere have no action on cupric oxide, which may begin to exert its catalytic action.

The temperature of decomposition of the nitrate may be calculated by means of Nernst's theorem (compare Brill, A., 1907, ii, 233), which gives $Q/4·571T = 4·4 \log T + 8·5$, where Q is the number

of cal. evolved during the reaction. For copper nitrate, Q is unknown, but Thomsen ("Thermochem. Unters.," 1906, 255) gave 95590 for the reaction $Cu + O_2 + N_2O_4 + 6H_2O$; if this value is increased by 12,900 cal., due to the dissociation of nitrogen peroxide into the dioxide, and diminished by 39,700 cal., due to the oxidation of the copper, the result is the heat of formation of the hexahydrated nitrate: $CuO + 2NO_2 + O + 6H_2O = Cu(NO_3)_2,6H_2O$. The value thus obtained requires diminution by the heat of hydration to yield the value of Q. The heat of solution of $Cu(NO_3)_2,3H_2O$ is -2550 cal., the values for the nearly anhydrous salts,

$$Cu(NO_3)_2,0{\cdot}52H_2O$$

and $Cu(NO_3)_2,0{\cdot}36H_2O$, being $+7813$ and $+8032$ cal. respectively; these numbers give the value 9488 cal. for the heat of solution of the anhydrous nitrate, whilst that of the hexahydrated salt is -10710 cal.

The heat of hydration of copper nitrate is, therefore, 20,198 cal., and $CuO + 2NO_2 + O = Cu(NO_3)_2 + 47{,}592$ cal. Insertion of $T = 523$ in the equation, $Q/4{\cdot}571T = 4{\cdot}4 \log T + 8{\cdot}5$, gives $Q = 48{,}917$ cal. The difference between the experimental and calculated values thus amounts to 2·6%, and is due partly to experimental error and partly to the approximate character of Nernst's formula.

T. H. P.

Synthermal Regulator, a Device for Automatically Maintaining an Adiabatic Condition in Calorimetry. Theodore W. Richards and George D. Osgood (*J. Amer. Chem. Soc.*, 1915, **37**, 1718—1720).—A description is given of an apparatus, termed a "synthermal regulator," for use in adiabatic calorimetry or for other work in which identical but changing temperatures are required in two contiguous vessels. It consists of a delicate differentical hydrogen thermometer with a sensitive mercury contact, which, with the help of a relay, enables a stronger current to operate a heating or cooling mechanism for causing one bath to follow the temperature of another within 0·03°. E. G.

Compressibilities of the Elements and their Relations to Other Properties. Theodore W. Richards (*J. Amer. Chem. Soc.*, 1915, **37**, 1643—1656).—The values obtained for the compressibilities of the elements (Richards, Stull, Brink, and Bonnet, A., 1907, ii, 858) have been reduced to the new standard for the compressibility of mercury (Richards and Bartlett, this vol., ii, 229). Attention is drawn to probable relations between the compressibilities and the atomic volumes, densities, coefficients of expansion, and m. p.'s and b. p.'s of many of the elements, and it is shown that the compressibilities can be calculated approximately from the atomic weights, densities, and m. p.'s by means of the equation

$$\beta = 0{\cdot}00021A/D^{1{\cdot}25}(T_m - 50°),$$

where β is the compressibility, A the atomic weight, D the density, and T_m the absolute m. p.

It has been found that at the same temperature liquids are much more compressible than the solids crystallised from them. Richards

and Speyers (A., 1914, ii, 261) have shown that the compressibility of ice is only about one-fourth of that of water at neighbouring temperatures. Solid *o*-cresol (D_{20} 1·0176) and *p*-cresol (D_{20} 1·389) have average compressibilities between 300 and 500 megabars of $23·8 \times 10^{-6}$ and $21·8 \times 10^{-6}$, whereas the compressibilities of these substances in the supercooled liquid state over the same range are $42·1 \times 10^{-6}$ and $41·8 \times 10^{-6}$ respectively. E. G.

Energy Changes of Binary Systems. II. Volume Changes and Heat Appearance in the Formation of Binary Mixtures. R. KREMANN, RUDOLF MEINGAST, and FRANZ GUGL (*Monatsh.*, 1914, **35**, 1235—1322. Compare Ehrlich and Kremann, A., 1907, ii, 747; Kremann, A., 1910, ii, 581).—The volume change, produced when binary mixtures of the following pairs of substances were made, has been measured: ethyl acetate, with methyl acetate, ethyl trichloroacetate, ethyl succinate, ethyl benzoate, amyl formate, *iso*amyl ether, and *n*-amyl acetate; propyl acetate and amyl formate; benzene with toluene and *m*-xylene; *m*-xylene with *o*-xylene and *p*-xylene; *p*-xylene and *o*-xylene; nitrobenzene with dimethylaniline, diethylaniline, monomethylaniline, and monoethylaniline; *m*-xylene and dimethylaniline; chlorobenzene and bromobenzene; *m*-cresol with benzene and toluene; nitrobenzene with aniline and *o*-toluidine; propyl alcohol and aniline; methyl alcohol and propyl alcohol; acetic acid with formic acid and *iso*butyric acid; and *m*-cresol with dimethylaniline and *o*-toluidine. The changes have been determined partly by measurement in a dilatometer and partly from density determinations. Very voluminous data and curves of the volume changes are given in the paper, together with density values and temperature-coefficients of the density. The heat change is determined for each of the above-mentioned binary mixtures, as well as the specific heat of the pure substances and the various binary mixtures. In a theoretical introduction it is shown that when heat is evolved on the mixing of two substances the components of the mixture are not normal in their behaviour, and when a heat absorption takes place the substances may be, but are not necessarily, normal. Normal behaviour is indicated when the observed ΔE value agrees with that calculated by the expression $\Delta E = n_1 . n_2 / b . (b_2\sqrt{a_1} - b_1\sqrt{a_2})^2 / b_1 b_2$, in which n_1 and n_2 are the number of molecules of the two components, and a_1, a_2, b_1 and b_2 the characteristic constants of the van der Waals equation. Normal behaviour is present when the heat change is zero, provided that both components have the same critical pressure. From the observed volume changes it is shown that the following binary systems are normal in their behaviour: propyl acetate–amyl formate; *m*-xylene–*o*-xylene; *m*-xylene–*p*-xylene; dimethylaniline–*m*-xylene, and *p*-xylene–*o*-xylene. The same result is also reached from considerations of the heat changes on mixing. J. F. S.

Changes of Volume Occurring in the Dissolution of Calcium Oxide and Hydroxide. A. CAVAZZI (*Gazzetta*, 1915, **45**, i, 529—533. Compare A., 1914, ii, 439).—One gram of calcium oxide,

when dissolved in 1 litre of water at 15°, produces a diminution in the volume of the solvent amounting to 0·7 c.c. From this result it is calculated that the specific gravity of the solution obtained is 1·0008265. Dalton found that 1 part of calcium oxide dissolves in 778 parts of water at 15°, so that 1 litre of water at 15° will dissolve 1·2842 gram. On the assumption that the contraction varies directly as the proportion of the oxide dissolved, the specific gravity of a solution of calcium oxide saturated at 15° is found to be 1·0014. One gram of calcium hydroxide, when dissolved at 15° in 1 litre of water, is found to reduce the volume of the latter by almost 0·5 c.c., this being slightly below the true value, since the conversion of a small proportion of the base into the carbonate could not be avoided.

The following are the contractions, in twentieths of 1 c.c., produced in 1 litre of water at 15° by 1 gram of various anhydrous salts: magnesium sulphate, 0·50; copper sulphate, 0·75; zinc sulphate, 0·81; sodium carbonate, 1·25; calcium oxide, 14·00. On the other hand, 1 gram of boron trioxide produces an increase in volume of approximately 6·87/20 c.c., which is equal to, or more or less greater than, that caused by 1 gram of potassium, sodium, or mercuric chloride, potassium iodide or chromate, or silver nitrate. Confirmation is thus afforded of the lability of the chemical linking between water and boric anhydride in solution.

One c.c. of calcium oxide, weighing 3·15 grams, yields 4·162 grams of the hydroxide, occupying 2·002 c.c. In practice, the expansive force exerted by this hydration is probably increased by the tenuity and discontinuity of the particles into which the lime is reduced on slaking, increased porosity resulting, and possibly also conditions favourable to augmented activity of the capillary phenomena observed in mortar. The importance with the latter of freedom from large proportions of free lime is thus rendered evident. T. H. P.

Spontaneous Ionisation of the Aqueous Vapour of the Atmosphere and its Importance in Natural Economy. II. Giuseppe Oddo (*Gazzetta*, 1915, **45**, i, 395—412).—The author discusses the various views which have been expressed concerning the origin of atmospheric electricity, this being connected largely, if not entirely, with the presence of water-vapour. The molecules of the latter, being in a rarefied or diluted state, undergo spontaneous ionisation in the same way as do electrolytes in dilute aqueous solution; the ionised aqueous vapour of the atmosphere acts, therefore, as a conductor of the second class. In comparison with this source of ions, all other sources, such as the actions of ultraviolet radiation from the sun and of terrestrial radioactive substances, etc., must be regarded as subsidiary.

From the specific humidity of the air, the number of molecules contained in one gram-mol. of a gas, and the numbers of ions formed from 100 mols. of water at different temperatures (*loc. cit.*), the ionic concentration is calculated for various temperatures and pressures. Fall of temperature diminishes the proportion of water-

vapour in the air, but, starting from 32°, increases its degree of ionisation. The calculations now made show that the ionic concentration, C_1, is highest and approximately constant between 5° and 20°; it remains high even at −10°, but diminishes rapidly between −10° and −20°, in spite of the rapid increase in the degree of ionisation; it is also high at 25°, decreasing rapidly at higher temperatures, and becoming virtually zero at 32°. With varying pressure, the ionic concentration changes nearly in accordance with Boyle's law, $p.C_1=K$.

It will be seen that the ionic concentration of the atmosphere is at its maximum for those conditions of temperature which are most suitable to animal and vegetable life, and it may be assumed that the latter constitutes a true indicator of this ionic concentration.

At 15° and a pressure of 760 mm., 1 kilogram of moist air, occupying 773·4 litres at 0° and 760 mm. in the dry state, contains 89×10^{-20} hydrogen and hydroxyl ions, and such marked ionisation would lead to the supposition that many processes of oxidation and reduction, occurring in contact with air, are electrolytic in character. A number of natural processes of the inorganic, vegetable, and animal kingdoms are discussed on these lines. T. H. P.

Adsorption in Solutions. VIII. The Law of Distribution. G. von Georgievics (*Monatsh.*, 1915, **36**, 391—405).—An account of work, some of which has been published previously (compare A., 1913, ii, 937). From the data obtained in measurements of the ratio of distribution of a number of fatty acids, chloro-substituted acetic acids, benzoic and salicylic acids between benzene and water, the author draws the conclusion that the distribution phenomena are not capable of explanation in terms of the partition law. The distribution between the two liquid layers is supposed to be analogous to those cases of distribution in which adsorption is involved.

In addition to the results obtained for monochloroacetic and dichloroacetic acids, the author gives data for the distribution of pyridine, piperidine, and hydrazine between benzene and water. In the case of these bases, the ratio of the concentrations is practically constant and independent of the absolute concentration. From this the conclusion is drawn that the affinity of water for the bases is less than that for the acids which have been submitted to examination. H. M. D.

Sorption of Some Acids and Non-electrolytes by Wool. A. Dietl (*Monatsh.*, 1914, **35**, 787—793).—The adsorption of phosphoric acid, benzoic acid, salicylic acid, acetone, and sucrose by wool has been determined at room temperature. The method consisted in allowing a measured volume of a solution of the above-named substances to remain in contact with a weighed quantity of wool for three to eight days. The amount adsorbed was then estimated by analysing the remaining solution. It is found that the three acids give small x values in the equation $\sqrt[x]{c_1/c_2}=K$, despite the fact that they are strongly adsorbed. This result is a

confirmation of Georgevic's statement (A., 1913, ii, 561) that the x value runs parallel with the strength of the acid. Acetone and sucrose have x values of 1·47 and 1·1 respectively, which points to the fact that the adsorption in these cases, which is very small, consists mainly in the formation of a solid solution. J. F. S.

The Kinetics of Sorption. A. Dietl (*Monatsh.*, 1914, **35**, 795—822).—The author has determined the rate of adsorption by wool at 20° of the following acids: hydrochloric, hydrobromic, nitric, sulphuric, phosphoric, formic, acetic, propionic, butyric, oxalic, and succinic. The solutions were measured at the concentrations 54·84, 13·71, and 2·742 millimolecular. The results are examined by means of the various formulæ which have been put forward to represent the velocity of adsorption. It is shown that the expression $dx/dt=k(a-x)$, due to Lagergren (*Bihg. Svenska Akad. Handl.*, 1898, **24**, 4 and 5), is only true in very few cases. Generally the constant calculated by means of this expression falls as the reaction proceeds. The various modifications of this expression, as well as equations representing the reaction as of the second order, and the equation $dx/dt=k(a-x)/x$, which states that the adsorbed material is inversely proportional to the velocity, also fail to give a constant. It is found that the reaction can be represented by making use of the equation for negative autocatalysis of the first order. This equation has the form $dx/dt=(k_1-k_2x)(a-x)$. The use of this equation is based on the assumption that as the adsorption proceeds the adsorbed substance produces a retardation of the diffusion, or that the decrease in concentration of the solution has a retarding effect on the velocity. In both cases the otherwise unimolecular reaction is retarded. J. F. S.

Drop Weight Method for the Determination of the Surface Tension of a Liquid. J. Livingston R. Morgan (*J. Amer. Chem. Soc.*, 1915, **37**, 1461—1468).—A résumé of the method of determining the surface tension of a liquid from the weight of a falling drop, and of the conditions on which it depends (compare A., 1908, ii, 356, 668; 1911, ii, 372, 584, 585, 698, 699, 857, 1067; 1913, ii, 833, 926, 1028; 1914, ii, 32, 33). E. G.

Surface Tensions of Water, Methyl, Ethyl, and *iso*Butyl Alcohols, Ethyl Butyrate, Benzene, and Toluene. Theodore W. Richards and Leslie B. Coombs (*J. Amer. Chem. Soc.*, 1915, **37**, 1656—1676).—There are considerable divergences in the values obtained for the surface tension of liquids by different observers and by different methods. The present investigation was undertaken with a view to discovering the causes of these divergences and to obtain accurate results for liquids already studied.

The determinations were made by measuring the rise of the liquids in capillary tubes, the following special precautions being taken. Inequalities in the glass tubes employed were detected and corrected by the use of reversible apparatus. The capillary rise was referred to an unrestricted flat surface, 38 mm. in diameter, it

having been found that smaller surfaces are not large enough, and that the insertion of a capillary into the middle of a larger tube causes appreciable error by increasing the capillary effect of the large tube. Care was taken that the true bottom of the meniscus should be read. The weight of the fine meniscus was allowed for, and a new formula suggested for its calculation, depending on the observed height of the meniscus.

The following values for the capillary constants at 20° were obtained: water, 14·861; benzene, 6·721; toluene, 6·743; methyl alcohol, 5·832; ethyl alcohol, 5·765; *iso*butyl alcohol, 5·823; ethyl butyrate, 5·704. E. G.

Energy Changes of Binary Systems. III. Surface Tension of Binary Mixtures. Robert Kremann and Rudolf Meingast (*Monatsh.*, 1914, **35**, 1323—1364. Compare this vol., ii, 519).—The surface tension of the pure liquids and binary mixtures mentioned in the previous abstract have been measured at a series of temperatures from 9·3° to 81° by the method of rise in capillary tubes. The molecular surface energy, $\gamma(Mv)^{\frac{2}{3}}$, and the temperature-coefficient of the molecular surface energy are calculated in each case. Curves of the relationship of the values of $\gamma(Mv)^{\frac{2}{3}}$ and of $d\gamma(Mv)^{\frac{2}{3}}/dt$ with molecular concentration are given in each case. In the case of the binary mixtures of esters it is shown that in every case the components behave normally, and that the factor $\gamma(Mv)^{\frac{2}{3}}$ is strictly additive. For mixtures of aromatic hydrocarbons the surface energy is shown to be additive and the mixtures to be slightly associated. All systems made up of one component known to be associated show themselves in the present case to be associated, and the same holds for mixtures of two associated liquids. Aniline and toluidine have been generally regarded as normal liquids; the present authors have found that they have abnormally low $d\gamma(Mv)^{\frac{2}{3}}/dt$ values, and consequently must be associated. This they have further investigated, and found that the freshly distilled liquids are normal, but if they are kept, even in absence of air and with no trace of darkening, they become abnormal. No relationship is found between the value of γ and the composition of the mixture, the curves for this relationship having generally the form of an *S*. It is shown that the presence of compounds in binary mixtures is made evident by the positive nature of the $\gamma(Mv)^{\frac{2}{3}}$ curve. J. F. S.

Energy Changes in Binary Systems. IV. Internal Friction of Binary Mixtures. R. Kremann, Fr. Gugl, and R. Meingast (*Monatsh.*, 1914, **35**, 1365—1385. Compare preceding abstract).—The viscosity of the binary mixtures mentioned in the previous abstract have been determined at temperatures from 11° to 77·5°. The results are given in tabular form, and also in curves. In only a few cases are the curves straight lines, thus showing the strict additive nature of the viscosity. These cases are: *o*-xylene and *p*-xylene at 12°; *p*-xylene and *m*-xylene at 12°; propyl acetate and amyl formate at 12° and 64°; acetic acid and formic acid at 11°

and 77°; and chlorobenzene and bromobenzene at 11·8° and 64°. In all other cases the curve is bent toward or away from the concentration axis. From this the authors draw the conclusion that with normal behaviour of the liquids in binary mixtures the curves as a rule are bent toward the concentration axis, and do not need to exhibit an additive behaviour. Mixtures in which the curve bends away from the concentration axis are generally associated or a compound is present, but this is not necessarily the case, because some mixtures known to be associated give curves which bend in the opposite direction. The mixture *m*-cresol–dimethylaniline is peculiar: at 9° it gives a curve which bends toward the concentration axis, but at 64° an *S*-formed curve is produced, so that one portion of the curve is bent toward the concentration axis and the other away from it, and at 77° a similar curve is obtained, but the point where it crosses the mean curve has advanced from about 20% dimethylaniline to 50%. J. F. S.

Relations between the Fusion and Viscosity Diagrams of Binary Systems. I. KURNAKOV, D. KROTKOV and M. OKSMAN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 558—588. Compare Kurnakov and Efremov, A., 1913, ii, 388; Kurnakov and Shemtschuschni, A., 1913, ii, 190).—The authors have compared the melting point and viscosity diagrams of the following binary systems: naphthalene with nitrobenzene, *m*-dinitrobenzene, and 1:3:5-trinitrobenzene; antimony trichloride with benzene, naphthalene, diphenylmethane, triphenylmethane, and aniline; and antimony tribromide with triphenylmethane, benzophenone, and acetophenone (compare Kremann, A., 1905, ii, 77; Menschutkin, A., 1911, i, 65, 273, 274; 1912, i, 98, 99, 100, 177, 193; 1912, ii, 920, 923).

The general conclusions drawn are as follows: The ratio of the maximum value of η for a binary system to the value of η for the more viscous component at the same temperature gives an indication of the stability of the compound formed in the liquid phase of the system. With the systems formed by antimony trihaloids with aromatic compounds, the lowest values of this ratio are given by the hydrocarbons, the system $CHPh_3$–$SbBr_3$, for example, giving the value 1·32 at 95°. Other values at the same temperature are: $COPh_2$–$SbBr_3$, 1·67; Ph·COMe–$SbBr_3$, 2·29; and NH_2Ph–$SbCl_3$, 24·71.

Compounds of naphthalene with nitro-derivatives of benzene exist only in the solid state, the viscosity isotherms indicating that they undergo dissociation to some extent on fusion. In the liquid systems formed by antimony trihaloids with aromatic hydrocarbons and their derivatives, the viscosity isotherms indicate clearly the mutual action of the components, the maxima of these isotherms being closely connected with the distectic points of the corresponding thermal diagrams (compare Menschutkin, *loc. cit.*). In certain cases the viscosity diagrams are of irrational type; as the temperature is lowered, the maxima of the viscosity isotherms undergo displacement towards the rational ordinates of the thermal distectics, whilst rise of temperature is accompanied by flattening

of the viscosity maxima and by their displacement towards the more viscous component. In the system triphenylmethane–antimony tribromide the viscosity isotherms indicate the formation in the liquid phase of a product of combination, which is not rendered evident by the melting-point diagram. T. H. P.

The Freezing-point Diagrams of Formamide with Water and the Aliphatic Acids and their Bearing on the Interpretation of Viscosity Measurements. SOLOMON ENGLISH and WILLIAM ERNEST STEPHEN TURNER (T., 1915, **107**, 774—783).—According to freezing-point measurements, formamide forms compounds with water and the aliphatic acids. Water, formic acid, and acetic acid each yield a single compound, the composition of which is given by the formulæ $H\cdot CO\cdot NH_2,H_2O$; $H\cdot CO\cdot NH_2,H\cdot CO_2H$, m. p. 1·1°; $H\cdot CO\cdot NH_2,2CH_3\cdot CO_2H$. Propionic and *n*-butyric acids each yield two compounds, represented by $H\cdot CO\cdot NH_2,Et\cdot CO_2H$; $2H\cdot CO\cdot NH_2,Et\cdot CO_2H$; $H\cdot CO\cdot NH_2,Pr\cdot CO_2H$; $2H\cdot CO\cdot NH_2,Pr\cdot CO_2H$.

The results of the freezing-point measurements are examined in reference to the viscosities of the several binary mixtures at 25° (compare Merry and Turner, T., 1914, **105**, 748). From this comparison the conclusion is drawn that although maxima on viscosity-composition curves may be due to chemical combination, the formation of compounds is not always accompanied by viscosity maxima. It is also pointed out that viscosity-composition curves do not afford evidence of more than one compound in binary mixtures which give rise to two or more according to the evidence of freezing-point measurements. The composition at which the viscosity shows a maximum deviation from that calculated according to the simple mixture rule is also found to deviate from that which corresponds with the compounds indicated by the freezing-point data. In the case of formamide–water mixtures, maximum deviation occurs at 40 instead of 50 mol. % of formamide, and for mixtures of formamide with acetic acid the maximum deviation lies at 50 instead of 33 mol. % of formamide. H. M. D.

Osmotic Pressure and Concentration in Solutions of Electrolytes, and the Calculation of the Degree of Ionisation. STUART J. BATES (*J. Amer. Chem. Soc.*, 1915, **37**, 1421—1445).—The divergence from Ostwald's dilution law exhibited by strong electrolytes may be due to the behaviour either of the ions or of the non-dissociated molecules, or of both. This behaviour may be expressed by the statement that van't Hoff's law, $\pi V = RT$, does not hold either for one or both of these molecular species.

The osmotic pressure of the ions and of the non-dissociated molecules in solutions of electrolytes has been calculated by means of conductivity data, together with measurements of one of the colligative properties, such as lowering of the f. p. and the *E.M.F.* of concentration cells. The osmotic pressure of the univalent ion is, in general, a little below that calculated from van't Hoff's law, whilst that of the non-dissociated molecules of strong uni-univalent

electrolytes is considerably greater, the deviation being about 15% in a concentration of 0·0001*N*. The bivalent ions deviate much more from van't Hoff's law than the univalent ions, whereas non-dissociated molecules of bi-bivalent salts obey the law fairly closely, the deviation being nearly constant between 0·001*N* and 0·02*N*. At concentrations up to 0·05*N* the various univalent ions show almost the same behaviour with respect to the relation between osmotic pressure and concentration, and the same is true of the bivalent ions. This relation may be expressed by an equation of the form $d\pi_i/dC_i = RT(1 + kC_i^m)$, and in dilute solutions a similar relation expresses the behaviour of the non-dissociated molecules. Hydration increases the osmotic pressure of both the ions and the non-dissociated molecules, but affects that of the latter more than that of the former, and therefore has some further effect than the removal of "free" water from the solution.

Applications of the empirical relation between osmotic pressure and concentration to various equilibria are pointed out, and that to *E.M.F.* phenomena is illustrated. E. G.

Hypothesis Concerning the Condition of Salts in Solution. A. N. Sachanov (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 434—439).—Various authors have advanced the view that the deviations exhibited by salts from the laws of van't Hoff may be explained as the result of hydrolysis of the salts under the influence of water. Bogorodski (this vol., ii, 418) assumes that a salt, MR, undergoes hydrolysis into the base combined with water, $M(OH)_n(H_2O)_x$, and the acid similarly combined, $RH_n(H_2O)_y$, such complexes being partly in mutual combination, so that chemical equilibrium is established between the dissociated and the undissociated molecules. The author considers this hypothesis in its relation to the value of van't Hoff's coefficient, *i*.

In the first place, it is natural to expect that salts of strong acids and strong bases would be decomposed to the least, and those of weak acids and weak bases to the greatest, extent, so that the values of *i* should be greatest in the latter case and least in the former. This is in direct contradiction to the experimental facts. Further, the above hypothesis indicates that deviations from van't Hoff's laws should be exhibited only by salts, whereas actually they are shown also by acids and bases. Rosenstiehl does, indeed, assume that acids and bases undergo hydrolysis, whilst others, including Bogorodski, suppose that acids and bases effect decomposition of polymerised water molecules into simple ones. It would follow, therefore, that dissolved salts should also effect such depolymerisation of water.

The agreement between the values of *i* obtained cryoscopically and those calculated by means of the equation $\alpha = (Q - q)/Q$, where α is the extent to which the molecules are decomposed hydrolytically, and Q and q respectively the heats of formation and neutralisation of the salt, is shown to be fallacious. Values of *i* are given without reference to the dilution, and, if the heat of neutralisation of an alkali by hydrochloric acid is taken as 68 or 274, instead of

the true value, 137, the values of i obtained from the above equation are 1·93—1·71, which also exhibit fictitious agreement with the actual values, 1·95—1·75, for binary salts at different dilutions. Further, the most exothermic salts of the alkali metals should give the highest values of i, which is not the case. For the great majority of salts, even the above fictitious agreement fails (compare Vilde and Bogorodski, this vol., ii, 512). T. H. P.

Chemistry. WILLIAM J. POPE (*Report Brit. Assoc.*, 1914, 322—335).—The address of the President of the Chemistry Section, dealing mainly with the application of crystallography to organic compounds, in connexion with stereochemistry. N. H. J. M.

Enantiomorphism of Molecular and Crystal Structure. WILLIAM BARLOW and WILLIAM JACKSON POPE (T., 1915, **107**, 700—702).—In a recent paper dealing with optical activity and enantiomorphism of molecular and crystal structure (T., 1913, **103**, 837) Barker and Marsh have drawn the conclusion that any assemblage of points possessing no other than digonal screw axes can only be associated with optical activity if the points themselves (that is, the molecules) are enantiomorphous. The authors consider that this statement is fallacious, and maintain that if the enantiomorphism of a crystal structure and the consequent optical activity are entirely traceable to an arrangement of points, located by coincidence movements about screw axes, the configuration of the component molecules is not enantiomorphous. At present there is no reason for attributing enantiomorphous molecular configurations to those compounds which are optically active in the crystalline form and optically inactive in the liquid state. H. M. D.

Structure of Crystalline Liquids. THE. SVEDBERG (*Kolloid. Zeitsch.*, 1915, **16**, 103—106).—The optical anisotropy, which is exhibited by crystalline liquids under the influence of a magnetic field, is found to be associated with changes in the electrical conductivity, the magnitude of which depends on the direction of the magnetic field relative to that of the applied electrical field. The anisotropy in the electrical conducting power increases with the strength of the magnetic field, at first slowly, then much more rapidly, afterwards more slowly, and tends towards a limiting constant value. In weak fields, a considerable interval of time elapses before the full effect is obtained. For a given magnetic field, the anisotropy depends on the temperature; as the temperature falls below the clearing temperature (the temperature at which the crystalline liquid is transformed into the ordinary isotropic modification), the anisotropy increases at first very rapidly, then more slowly, and ultimately varies with the temperature according to a linear equation. H. M. D.

The Relations between the Tyndall Effect and the Size of the Particles in Colloidal Solutions. WERNER MECKLENBURG (*Kolloid. Zeitsch.*, 1915, **16**, 97—103).—By means of the apparatus

described in a previous paper (A., 1914, ii, 445), experiments have been made with colloidal solutions of sulphur in order to ascertain the dependence of the Tyndall effect on the concentration of the solution, the size of the colloidal particles, and the wave-length of the incident light. By a process of fractionation, a series of nine solutions was obtained, each containing particles of approximately the same size, which varied from a diameter $=5\,\mu\mu$ at the one end to $840\,\mu\mu$ at the other end of the series.

For solutions containing particles of the same size the intensity of the Tyndall effect is proportional to the concentration of the solution. For solutions which contain particles of diameter less than $100\,\mu\mu$, the intensity of the effect is inversely proportional to the fourth power of the wave-length, whilst for particles of diameter between 250 and $850\,\mu\mu$, the intensity varies inversely as the square of the wave-length. Neither the Rayleigh relation ($I.\lambda^4=c$), nor the Clausius relation ($I.\lambda^2=c$) is satisfied in the case of solutions which contain particles of diameter between 100 and $250\,\mu\mu$, and the results indicate a gradual transition from the one group to the other as the size of the particles changes.

It is shown that the measurement of the Tyndall effect may be applied to the determination of the relative size of the particles in monodisperse solutions of varying degrees of dispersity. H. M. D.

Forms of Growth Resembling Living Organisms and their Products Slowly Deposited from Metastable Solutions of Inorganic Colloids. Benjamin Moore and W. G. Evans (*Proc. Roy. Soc.*, 1915, [*B*], **89**, 17—27).—Colloidal solutions may be prepared which are only slowly influenced by a change in the external conditions. The passage of a hydrosol into a hydrogel may be preceded for a long time by a metastable condition of the colloidal solution. The forms assumed by the depositions, or growths, from such slowly changing metastable colloidal solutions sometimes closely resemble lowly living organisms.

The metastable colloidal solutions employed by the authors are prepared from ferric nitrate and sodium silicate in such proportions as to give a slight deposit after boiling for ten minutes. The solution then contains two metastable colloids, ferric hydroxide and silicic acid. Solutions giving no deposit after boiling, or those which, on the other hand, are completely deposited, do not form growths. The colloidal solution is then placed in sterilised tubes, which, after being hermetically sealed, are heated in an autoclave for fifteen minutes at 110°. After seven months the tubes are opened and the contents examined microscopically. Microphotographs are given of the growths in the tubes, which consisted of (1) patches of sometimes fine, sometimes coarse granular deposits with fine fibres running in them; (2) chains of dots, sometimes slightly elongated, like micrococci or short bacteria; (3) branching, coarse fibres like hyphæ of a fungus; (4) long, coarse fibres like cotton fibres; (5) excessively fine fibrils, sometimes forming a network like a fibrin network; at other times they are single and convoluted into the most intricate knots or loops. These deposits

are stained by dyes like methylene-blue, and do not give the reaction with iodine and sulphuric acid for cellulose.

Another metastable solution employed is prepared from sodium silicate and dilute phosphoric acid, and contains metastable, colloidal silicic acid. The deposits obtained are similar in form to those already described, but not so numerous.

The living cell is built up of metastable colloids, but the authors state that they were unable to observe anything which could be described as a living organism arise from the inorganic solids they have investigated. It was not found possible to subculture any of the growths in other media. H. W. B.

Production of Growths or Deposits in Metastable Inorganic Hydrosols. Benjamin Moore (*Proc. Roy. Soc.*, 1915, [*B*], **89**, 27—35. Compare preceding abstract).—Successful attempts have been made by the author to obtain growths, similar to those described in the preceding abstract, in a few minutes instead of several months. Positive results were obtained (1) by using stronger solutions of ferric nitrate and sodium silicate, (2) by mixing two colloidal solutions of opposite cataphoresis (ferric hydroxide and silicic acid) until the point of permanent precipitation was just being reached, (3) by mixing solutions of colloidal ferric hydroxide and colloidal sulphur, and (4) by dialysing colloidal silicic acid prepared from sodium silicate and hydrochloric acid, when the growths appear whilst the solution is still perfectly mobile. In the first three cases, the growths appear almost immediately after the solutions are mixed, and consist of a network of fibres, some of which are exceedingly fine, whilst some of the medium-sized fibres have branches and show nodulation, cross-striations, or divisions. They often closely resemble the hyphæ of a fungus. The actual mode of growth of the fibres has not been ascertained. Some of the experiments have been carried out with all possible precautions taken to exclude contamination by micro-organisms. In these circumstances the growths are still observed, but the network of fibres is usually of finer texture. H. W. B.

Dyes. I. Traube and F. Köhler (*Inter. Zeitsch. phys.-chem. Biol.*, 1915, **2**, 197—226).—Previous experiments (this vol., ii, 154) on the influence of foreign substances on the rate of gelatinisation of gelatin solutions, and also on the rate of liquefaction of the gel, have been extended to various dyes. In general, basic dyes give rise to a decrease in the rate of liquefaction and an increase in the rate of gelatinisation. These effects are more pronounced with dyes of marked colloidal character. Acid dyes in most cases increase the rate of liquefaction, and reduce the rate of gelatinisation. According to this, acid dyes generally exert a swelling effect, but exceptions have been found.

Experiments on the diffusion of dyes in gelatin jellies show that the rate of diffusion runs more or less parallel with the permeability as exhibited in experiments with plant cells. In most cases the rate of diffusion appears to be determined by the size of the colloid particles, but this is not always so.

The authors call attention to the importance of the relations referred to in connexion with various biological problems.

H. M. D.

Theory of Dyeing. J. Traube (*Ber.*, 1915, **48**, 938—946).—A study of the effects of various dyes on the swelling of gelatin has led to interesting conclusions with regard to the theory of dyeing. The details of the experiments with sixty-five different dyes will be published in another place; a summary of the chief results is given in this paper.

The method adopted was to measure the speed at which the jellies re-dissolved at a given temperature, the sinking of small glass beads being taken as the critical point. It is found that, generally speaking, basic dyes like night-blue, hinder the re-solution of the gel, whilst acid dyes like benzopurpurin and anthraquinone-green promote the swelling and solution. The degree of the action of the dye depends on its colloidal character; highly colloidal dyes like night-blue, Victoria-blue, naphthindone, and new-blue have pronounced effects, whilst dispersoid dyes like methylene-blue have scarcely any action. Dyes which hinder imbibition tend to deposit on the surface of the swollen gel, the more so the more colloidal they are, whilst dyes which promote swelling spread into the gel.

The last point was studied in a series of test-tube experiments on the rate of diffusion of 0·1% solutions of dyes into 10% gelatin jelly. Highly colloidal dyes did not enter the gel at all, whilst highly disperse dyes diffused to a depth of 10—16 mm. in a day, and the solutions of the colloidal dyes were decolorised in a few days, nearly all the dye appearing as a thick crust at the surface of the gel. This is regarded as a true picture of the process operative in dyeing. If the fibres are sufficiently swollen and the dye is sufficiently colloidal, adsorption at the surface of the fibre takes place. The addition of salts, acids, alkalis, and mordants (A., 1912, ii, 740) is discussed, and experimental evidence is adduced in support of the following points. The addition of bases to basic dyes and acids to acid dyes works favourably by increasing the size of the particles of the dye (this vol., i, 105), and also by promoting the swelling of the fibres. Sodium sulphate hinders the gel from re-dissolving.

It is suggested that by diffusion experiments in test-tubes the most advantageous addition of a salt, acid, or base may be ascertained very readily.

J. C. W.

New Type of Action in Chemical Precipitation. Raphael Ed. Liesegang (*Chem. Zentr.*, 1914, ii, 1260; from *Arch. Entwicklungsmechanik Organismen*, 1914, **39**, 362—374).—When solutions of silver nitrate and potassium dichromate travel towards one another in a layer of jelly, peculiarly formed precipitates of silver chromate separate in the intervening space. The forms undergo a characteristic change when small quantities of acid are added to the jelly.

H. W.

Theory of Emulsification. VII. Wilder D. Bancroft (*J. Physical Chem.*, 1915, **19**, 513—529. Compare A., 1913, ii, 121, 680).—The formation of solid films on colloidal solutions is dis-

cussed in the present paper. The experimental work of Metcalf (A., 1905, ii, 512) and some new experiments by the author with solutions of pepsin-fibrinogen-peptone-α constitute the basis of the discussion. It is shown that the Gibbs theorem in regard to the concentration in the surface film of substances which lower the surface tension applies only to substances in true solution. Since peptone does not dissolve in water to any appreciable extent, the concentration of peptone in the surface film does not give rise to the enormous differences of osmotic pressure calculated by Metcalf. Whilst the presence of adsorbed gases may be a factor in causing the formation of a solid film, it is not the sole factor, and is probably a minor factor in most cases. The solid film which forms over mercury is an oxide, and the films formed over ferric chloride solutions are hydrated ferric oxide. There is no reason for postulating the formation of an insoluble modification with peptone. The peptone particles concentrate in the surface, and coalesce to form a solid film. A similar result can be obtained with colloidal silver. The formation of a solid film at the surface of a liquid is an intermediate case between the adsorption of solids at a dineric interface and the flotation of solids by adsorbed gases. J. F. S.

Experiments on Emulsions. II. T. Roland Briggs and Hugo F. Schmidt (*J. Physical Chem.*, 1915, **19**, 478—499. Compare Newman, A., 1914, ii, 183).—The conditions of formation of benzene emulsions in water and water emulsions in benzene in the presence of sodium oleate, sodium resinate, ferric acetate, gelatin, and gum arabic have been studied. It is shown that two types of emulsions are possible with benzene and water depending on the nature of the emulsifying agent and the properties of the films produced in the dineric interface. Emulsions of benzene in water may be prepared if a suitable emulsifier, which is soluble in water, is present; under these conditions the relative amounts of the two phases and the wetting of the walls of the bottle are of very little importance in determining the type of the emulsion. Emulsions of benzene in water may be obtained by direct shaking in the presence of small amounts of alkali soaps and other substances. The concentration of benzene in the emulsion varies with the amount and intensity of shaking, and approaches a limit which is probably not much below 100%. From experiments with different emulsifying agents it is shown that the properties of the emulsion depend largely on the interfacial membrane. The ease with which benzene is emulsified in aqueous sodium oleate solutions increases very rapidly at first as the concentration of the soap rises to 0·01%, after which it remains more or less constant. The ease with which benzene is emulsified in aqueous solutions of sodium oleate is strongly influenced by free alkali hydroxide, which has a peptonising action at low concentrations. Emulsions of water in benzene may be prepared if a suitable emulsifying agent is present; under these conditions the relative amounts of the two phases and the wetting of the walls of the bottle are of secondary importance in determining the type of emulsion. The nature of the emulsions

of water in benzene depends on the properties of the film produced in the dineric interface. The drop number cannot be used directly as a measure of the probable efficiency of a substance as an emulsifying agent for a given liquid. J. F. S.

Criticism of Gurvitsch's Hypothesis of a Physico-chemical Force of Attraction. N. A. Kolosovski (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 717—723).—The author regards Gurvitsch's hypothesis (A., 1914, ii, 435) as unfounded, and shows that the results expressing the distribution of valeric acid between light petroleum and sulphuric acid are in accord, not only with the arbitrary equation suggested by Gurvitsch, but also with the theoretical formulæ of Freundlich and of Nernst.

Gurvitsch's numbers lead to the striking fact that the distributions of benzoic and valeric acids between light petroleum and floridin are expressed by one and the same equation, $y=5{\cdot}38p^{0{\cdot}086}$, the coefficient of distribution, $K^{1/m}$, having the value 0·186 in each case. No theoretical significance is suggested for this coincidence. T. H. P.

New Method of Finding the Second Dissociation Constants of Dibasic Acids. Aswini Kumar Datta and Nilratan Dhar (T., 1915, **107**, 824—827).—The method is based on the fact that a solution of the sodium salt of a dibasic acid dissolves more carbon dioxide than an equal volume of water. Experimentally the determination is carried out by connecting in series a 250 c.c. Erlenmeyer flask, containing water, two U-tubes containing calcium chloride, a second similar Erlenmeyer flask containing the solution, two more U-tubes, and a guard-tube. The individual parts of the apparatus and their contents are weighed, carbon dioxide is then passed through for about one and a-half hours, and the various parts are then re-weighed; from the increase in weight of the various parts the increased solubility is deduced. If a is the concentration of carbon dioxide in water, s that dissolved in the salt solution of concentration c, then k, the second dissociation constant, is given by $a\times 3\times 10^{-7}\times\{c-2(s-a)\}/(s-a)^2$, where 3×10^{-7} is the first dissociation constant of carbonic acid (Walker, A., 1900, ii, 268). The following values of $k.10^6$ are found at 25°: tartaric acid, 99; succinic, 4·5; malonic, 1·9; oxalic, 38·5; fumaric, 36·1; malic, 13·0; and phthalic, 2·5. J. F. S.

Investigations on Ammonia. II. New Determination of the Ammonia Equilibrium at 30 Atmospheres Pressure. F. Haber, S. Tamaru, and Ch. Ponnaz (*Zeitsch. Elektrochem.*, 1915, **21**, 89—106. Compare this vol., ii, 226).—The equilibrium between nitrogen, hydrogen, and ammonia has been reinvestigated at temperatures between 550° and 1000° and 30 atmospheres pressure. Osmium was used as catalyst, and both external and internal methods of heating were applied. The details of apparatus and the experimental method are in general the same as previously described (*loc. cit.*, and Haber and Le Rossignol, A., 1907, ii, 454;

1908, ii, 362, 819). It is shown that the new determinations are in complete agreement with the previous work, and can be expressed along with the earlier measurements by the expression:

$$\log k_p = 13200/4{\cdot}571T - 6{\cdot}134,$$

in which k_p is given by the expression $k_p = P_{NH_3}/p_{H_2}^{3/2} \cdot p_{N_2}^{1/2}$.

J. F. S.

Equilibrium in the System Disodium Hydrogen Arsenate, Lead Nitrate, and Water at 25°. E. E. Curry and T. O. Smith (*J. Amer. Chem. Soc.*, 1915, **37**, 1685—1688).—During an investigation of commercial lead arsenates, the authors experienced the need of definite information regarding the theoretical compounds of lead and arsenic acid, the compounds described in the literature having been obtained under ordinary synthetic rather than equilibrium conditions. A study was therefore undertaken by the solubility method to determine the compounds existing at 25° in the system disodium hydrogen arsenate, lead nitrate, and water. The results have shown that only one compound exists under these conditions, namely, lead hydrogen arsenate. E. G.

Solubility Curves of Salt Hydrates: Calcium Nitrate. Hugh Stott Taylor and William Noland Henderson (*J. Amer. Chem. Soc.*, 1915, **37**, 1688—1694).—Bassett and Taylor (T., 1912, **101**, 576) have studied the two-component system, calcium nitrate–water. Hasselblatt (A., 1913, ii, 484) has obtained evidence of the existence of two forms of the tetrahydrate, m. p. 42·6° and 39·7°, the former agreeing with that obtained by Bassett and Taylor. A study has now been made of the solubility curve of the unstable calcium nitrate tetrahydrate in order to complete the phase diagram already established, and it has been found that this shows a maximum solubility corresponding with the solid phase at 39·7°, the m. p. of the substance, as well as a retroflex portion of the curve.

According to the results obtained by D'Ans and Siegler (A., 1913, ii, 214), the curve of the anhydrous salt in the unstable region should show a sharp change of direction below 50°, or, in other words, the heat of solution in the almost saturated solution must undergo a sudden change in the region 25—50°. As this seemed improbable, the solubility of the anhydrous salt at 25° has been determined, and it has been found to correspond with those obtained by Bassett and Taylor at the higher temperatures, and not with that obtained by D'Ans.

The stable solubility curve of Bassett and Taylor has been reinvestigated, and in one or two cases small changes in the solubility values have been made. E. G.

The Hypohalogenous Acids and the Hypohalogenites. VIII. The Temperature-coefficient of the Reciprocal Reactions of the Iodine-Iodate Equilibrium. Anton Skrabal (*Monatsh.*, 1914, **35**, 1157—1234. Compare A., 1907, ii, 448; 1909, ii, 224; 1911, ii, 382; 1912, ii, 33, 340; 1914, ii, 623).—The velocity of

formation of iodate from iodine and iodide in a mixture of sodium carbonate and hydrogen carbonate solutions has been determined at 18°, 25·3°, and 32·5°, and the temperature-coefficient calculated to 45·0 as a mean. When a similar reaction was effected in sodium acetate solution the temperature-coefficient had the value 2·0. The velocity of decomposition of iodate in a mixture of acetic acid and sodium acetate solution determined at 18° and 32·8° leads to the temperature-coefficient 1·34. The same reaction in a mixture of disodium and monosodium phosphates at 18·0°, 25·0°, and 35·0° gives a temperature-coefficient of 1·26; in a mixture of potassium fluoride and hydrogen fluoride at 14·0°, 25·0°, and 35·0° a value of the temperature-coefficient of 0·9—1·04 is obtained, a mixture of sodium sulphate and hydrogen sulphate at 17·5° and 31·5° leads to a value of 0·85, and at 80° to a value 0·83. The temperature-coefficient of reactions is considered theoretically at great length in the paper. It is shown that the temperature-coefficient $k_{t+10} : k_t$ of a reaction must necessarily undergo a change when the substances, which affect the time equation, are transformed into complexes. The relationship between the temperature-coefficient τ of the original reaction and τ', that of the reaction between the complex substances, is governed by the formula:

$$\tau'/\tau = e^{10/RT(T+10)(mQ_1+nQ_2+\ldots+xq_1+yq_2+\ldots)} \quad . \quad . \quad . \quad \text{(i)}$$

in which Q and q represent the heat changes of the complex reaction, and the sum $(m+n+\ldots+x+y+\ldots)$ indicates the order of the reaction. With the change of the temperature-coefficient a change occurs in the heat change of the total reaction. If Q is the heat change of the original reaction, then U, the heat change of the reaction between the complex substances, is given by the equation:

$$U = Q - (aQ_1 + bQ_2 + cQ_3 + \ldots) \qquad \text{(ii)}$$

where a, b, and c are the molecular coefficients of the substances in the total reaction. Formula (i) indicates that a great variability of τ is to be expected with reactions of the higher orders, and this has been proved in the present paper for the two reversible reactions: $3I_2 + 6OH' \rightleftarrows 5I' + IO_3' + 3H_2O$, and

$$IO_3' + 5I' + 6H^{\cdot} \rightleftarrows 3I_2 + 3H_2O,$$

of the equilibrium of iodate-iodide. The observed temperature-coefficient and that calculated by formula (i) are in good agreement, and in this connexion it has been shown that the limits 1—7 previously observed for the temperature-coefficient can be enlarged to a great extent, for values of 0·8 and 100 have been experimentally observed. In the case of the value 0·8 a reaction has been observed and measured for the first time, in which the velocity definitely decreases with increase of temperature. The discussion of formulæ (i) and (ii) leads to the following general results: (*a*) immeasurably rapid reactions have a temperature-coefficient of unity; (*b*) the temperature-coefficient is greater the smaller the velocity and the less exothermic the reaction; (*c*) large temperature-coefficients of the order 100—1000 are found in very slow, strongly endothermic reactions, and those in the region of

unity are found with very rapid, strongly exothermic reactions, exception being made in the case of reactions of medium velocity and high positive heat change. The relative scarcity of fractional temperature-coefficients and the probable non-existence of very small coefficients of the order 0·01—0·001, are probably to be attributed to the frequency with which the Berthelot principle holds at medium temperatures. The original temperature-coefficient rule is the most generally observed case, and it is only true for easily measurable reactions, and for reactions of approximately the same velocity. Finally, it is shown that the relationships which exist between the temperature-coefficient, the velocity, and the heat change of reactions are such that they must regulate the velocity of reactions on the side of smaller velocities in the case of both isothermal and adiabatic reactions. J. F. S.

Some Double Decompositions of Calcium Thiosulphate which occurs as a By-product in the Leblanc Soda Process from the Points of View of the Law of Mass Action and the Phase Rule. ROBERT KREMANN and HANS RODEMUND (*Monatsh.*, 1915, **35**, 1061—1113).—The alkali waste from the Leblanc soda process is converted into calcium thiosulphate, and this substance by means of sodium sulphate or sodium carbonate into sodium thiosulphate. The author considers these two reactions on the basis of the law of mass action. In the theoretical consideration some of the necessary data are unknown, and these have been experimentally determined. It is shown that calcium thiosulphate dissolves to the extent of 29·4 parts at 9° and 34·7 parts at 25° in 100 of water, and that it is dissociated in saturated solution to the extent of about 0·6% at both temperatures. Using these figures and other known data, the mass action constant is calculated for the double decompositions:

(1) $$CaS_2O_3 + Na_2CO_3 \rightleftarrows Na_2S_2O_3 + CaCO_3,$$

and

(2) $$CaS_2O_3 + Na_2SO_4 \rightleftarrows Na_2S_2O_3 + CaSO_4.$$

It is found that $k_2^{9°} = 2·06 \times 10^4$ and $k_2^{25°} = 3·17 \times 10^4$, $k_1^{9°} = 7·94 \times 10^7$ and $k_1^{25°} = 9·475 \times 10^7$, from which it follows that the reaction with sodium carbonate will give a much better yield of sodium thiosulphate than the other reaction. The theoretically deduced results are examined experimentally. Quantities of calcium thiosulphate are shaken with the requisite quantities of 0·5, 0·8, and 1·3*N*-solutions of sodium sulphate and sodium carbonate, and the extent of reaction, *i.e.*, the amount of sodium thiosulphate formed, is deduced by titrating the solution with iodine. In both cases and at the two temperatures 9° and 25°, it is shown that the maximum quantity of sodium thiosulphate is not formed. However, attempts to reach the equilibrium point, if such exists, by shaking sodium thiosulphate with calcium sulphate or calcium carbonate show that the maximum quantity of thiosulphate should have been produced in the first experiments. The incomplete formation (97—98%) of sodium thiosulphate in the first experiments is due to

the formation of calcium sulphate and calcium carbonate respectively on the grains of calcium thiosulphate, which thereby prevent further action. The double decomposition:

$$2NaNO_3 + CaS_2O_3 \rightleftarrows Na_2S_2O_3 + Ca(NO_3)_2,$$

is studied from the point of view of the phase rule. The method consisted in weighing out such quantities of the salts that one, two, or three remained in the solid phase, and determining the concentration of the four salts in the saturated solution at 9° and 25°. The results were plotted on a co-ordinate system, consisting of the projection of the four edges of a regular octahedron. It is shown that no double salts of any of the pairs of salts exist in the temperature region examined, but that a triple salt,

$$NaNO_3,CaS_2O_3,Na_2S_2O_3,11H_2O,$$

exists. This salt is stable up to about 33°, and has the following solubility values calculated in grams of anhydrous salt in 100 grams of solution: 1°, 42·14; 9°, 43·61; 15°, 46·29; 20°, 50·40; 25°, 56·28; 27°, 58·86; 28°, 60·99; and 30°, 63·30. The salt exists in silky needles, which are quite different in appearance from the mixture of the constituent salts. The transition point has been determined by the solubility method and by the thermometric method. The transition,

$$NaNO_3,CaS_2O_3,Na_2S_2O_3,11H_2O \rightleftarrows NaNO_3 + CaS_2O_3,6H_2O + Na_2S_2O_3,5H_2O,$$

takes place at 29·2°. This is the only known case of the existence of a triple salt, the constituents of which do not form double salts.

J. F. S.

Natural Fats from the Point of View of the Phase Rule. IV. The Ternary System Tristearin – Tripalmitin – Stearic Acid. R. Kremann and R. Kropsch (*Monatsh.*, 1914, **35**, 823—839. Compare A., 1914, ii, 637).—The binary systems which comprise the present ternary system have been previously examined. In the present paper constant mixtures of each pair of the three components are taken, and various quantities of the third component are added to each mixture, and the points of crystallisation or solidification are measured. Curves are given expressing the relationships observed, and the whole of the results are plotted on a triangular co-ordinate system. J. F. S.

Natural Fats from the Point of View of the Phase Rule. V. The Ternary System Tristearin – Tripalmitin – Palmitic Acid. R. Kremann and R. Kropsch (*Monatsh.*, 1914, **35**, 841—857. Compare A., 1914, ii, 637, and preceding abstract).—This system is examined in exactly the same way as indicated (*loc. cit.*), and the relationships obtained are represented on a triangular co-ordinate system, which is considerably more complicated than the system previously examined. J. F. S.

Kinetics of the Bromate-Nitrite Reaction. ALBIN KURTENACKER (*Monatsh.*, 1914, **35**, 925—944).—The reaction between bromate and nitrite follows the three simple reactions:

(1) $BrO_3' + 3NO_2' = Br' + 3NO_3'$,

(2) $BrO_3' + 5Br' + 6H^{\cdot} = 3Br_2 + 3H_2O$,

and (3) $Br_2 + NO_2' + H_2O = 2Br' + NO_3' + 2H^{\cdot}$.

In the present paper, reaction (1) is considered. This is achieved by allowing the bromate and nitrite to react in a feebly acid solution. Solutions of known concentration of potassium bromate and potassium nitrite were brought together in the presence of dilute acetic acid at 21°. After the reaction had proceeded for a sufficiently long time it was stopped by the addition of so much sodium hydroxide solution that 75% of the acetic acid was neutralised. The unused nitrite was then decomposed by the addition of bromine water, the excess of bromine being reduced by the addition of 0·01*N*-thiosulphate. Potassium iodide was then added, and any liberated iodine reduced by a drop of 0·01*N*-thiosulphate. Then hydrochloric acid was added, and the bromate decomposed with the liberation of iodine, which was estimated by a 0·1*N*-thiosulphate solution and the amount of bromate present calculated. Each estimation, it will be seen, requires a fresh quantity of the solution. The reaction is shown to be of the first order with respect to the bromate. The reaction is very slightly influenced by the concentration of the nitrite, and only when the relation of the concentration of bromate to nitrite is very large or equal to unity. With large concentrations of nitrite the velocity is independent of the nitrite concentration, and in this case the reaction is of the first order. The velocity is strongly accelerated by acetic acid. The behaviour of the nitrite and the acetic acid is explained by the assumption that the reaction which has been measured consists in the interaction of bromic acid and nitric oxide, and in which the nitrous acid is only so far active as it produces the nitric oxide as fast as it is used up. So that the reaction (1) is to be regarded as made up of the two actions, (1*a*) $3NO_2' + 2H^{\cdot} = 2NO + NO_3' + H_2O$, and (1*b*) $BrO_3' + 2NO + H_2O = Br' + 2NO_3' + 2H^{\cdot}$. J. F. S.

Steric Influence: Static and Dynamic. II. OLIVER CHARLES MINTY DAVIS and FREDERIC WILLIAM RIXON (T., 1915, **107**, 728—736. Compare A., 1912, ii, 32).—In order to obtain information relative to steric effects in the formation and decomposition of formanilide and the corresponding compounds obtained from aniline derivatives, the authors have made experiments in which they measured (1) the velocity of formation of the anilide, (2) the velocity of decomposition, (3) the equilibrium ratio. The solvent consisted of a mixture of two volumes of pyridine with one of water, and the measurements were made at 100°. The reaction velocities are expressed in terms of empirical coefficients.

The results obtained show that the velocity-coefficients obtained in the first series of experiments run approximately parallel with

the percentage amounts of the anilide formed in the condition of equilibrium. The influence of the nature of the substituent and of ortho-, meta-, and para-isomerism is discussed in reference to these data. H. M. D.

Studies on the Walden Inversion. II. The Kinetics and Dissociation Constant of Phenylchloroacetic Acid. GEORGE SENTER (T., 1915, **107**, 908—915. Compare T., 1907, **91**, 460; 1909, **95**, 1827; 1910, **97**, 346).—The hydrolysis of phenylchloroacetic acid as represented by the equation:

$$CHPhCl\cdot CO_2H + H_2O \longrightarrow OH\cdot CHPh\cdot CO_2H + HCl,$$

has been investigated. It is shown that the hydrolysis is mainly effected by the action of water on the anion, very little occurring with the non-ionised acid. The latter point is proved by the diminution of the velocity constant when the reaction is carried out in the presence of hydrochloric acid of various concentrations. A further series of experiments are described on the hydrolysis of the sodium salt of phenylchloroacetic acid by water and by sodium hydroxide. The reaction is shown to be the same as in the previous case; further, it is shown that the hydroxyl ions from the sodium hydroxide have an action which is quite negligible in comparison with the action of water. The presence of sodium chloride has a slight accelerating influence on the hydrolysis of the sodium salt of phenylchloroacetic acid. In order to make the necessary calculation the degree of dissociation of the acid was necessary. The author has therefore made a series of electrical conductivity measurements at 25°, and calculated this value on the assumption that $\Delta_\infty = 377$. The temperature-coefficient of the hydrolysis has the value 3·6 between the temperatures 25° and 50·1°. J. F. S.

Methyl Salicylate. IV. The Saponification of Methyl Salicylate, Methyl Benzoate, and Methyl *o*-Methoxybenzoate. H. D. GIBBS, R. R. WILLIAMS, and A. S. GALAJIKIAN (*Philippine J. Sci.*, 1913, **8**, 1—30. Compare A., 1908, ii, 906; 1909, i, 231; 1912, ii, 1119).—The rate of saponification of the esters was measured in experiments in which the esters were present in excess, forming a second layer of liquid. In these circumstances the concentration of the ester in the aqueous solution remains constant, and the saponification proceeds in accordance with the requirements of the equation for a unimolecular change. At 30° the values obtained for the velocity-coefficient are as follows: methyl benzoate, 4·529; methyl salicylate, 6·36; methyl *o*-methoxybenzoate, 2·029; sodium derivative of methyl salicylate, 0·1605. The first and the third were also investigated in homogeneous solution, giving 5·411 and 2·593 respectively for the (bimolecular) velocity-coefficient.

According to conductivity measurements, the ionisation constant of methyl salicylate at 30° is of the order 10^{-11}, which agrees with the value calculated from the hydrolysis of the sodium derivative of methyl salicylate ($k_h = 0·001$). The hydrolysis of pure aqueous solutions of methyl salicylate has also been examined by measuring the increase in the electrical conductivity of the solutions, and the

paper contains data obtained at 30° and 100°. Saturated aqueous solutions at 30° contain per litre 0·01568 mol. of methyl benzoate, 0·0371 of the methyl *o*-methoxybenzoate, and 0·005 mol. of methyl salicylate. H. M. D.

Temperature-coefficients and the Effects of Acids, Bases, and Salts on Velocities of Reaction of the Triphenylmethane Dyes. H. C. Biddle and C. W. Porter (*J. Amer. Chem. Soc.*, 1915, **37**, 1571—1589).—Biddle (A., 1913, ii, 312; 1914, ii, 115) has shown that the equilibrium between the coloured and colourless forms of triphenylmethane dyes is largely dependent on the concentration of the hydrogen ions of the acid, and he has studied the influence of neutral salts on the rate of reaction. Adams and Rosenstein (A., 1914, i, 1092) have investigated the rate of fading of crystal-violet in acid solution. The present work was undertaken to ascertain the influence of temperature on the velocity of the colour changes, to determine more fully the effect of varying concentrations of acids and bases on these changes, and to obtain further data on the neutral salt effect.

The temperature-coefficient for the conversion of a triphenylmethanecarbinol into the quinonoid form in presence of an acid is independent of the concentration of the acid, and also independent of the temperature (between 25° and 40°). In the case of crystal-violet, the velocity of the change increases 66% for each 5°. Changes of the same order of magnitude have been observed with the diamino-derivatives. The temperature-coefficient of the rate of fading of a triphenylmethane dye in presence of alkali is independent both of the concentration of the alkali and of the temperature (between 25° and 40°). The increase of velocity in the case of crystal-violet is 43% for each 5°.

For concentrations of acid below 0·024*N* the rate of development of colour in crystal-violet is an inverse function of the $H^{\cdot}$ ion-concentration, but for higher concentrations of acid it is a direct function of the $H^{\cdot}$ ion-concentration. The rate of fading is a direct function of the concentration of the OH' ions, and, in the case of basic dyes, such as crystal-violet, is exactly proportional to such concentration.

Neutral salts retard the rate of fading and of development of colour in all the basic triphenylmethane dyes, but accelerate the rate of fading in the case of acidic dyes. All uni-univalent neutral salts in equivalent concentrations are equally effective in modifying the catalytic influence of the acid or base; they behave like acids in their effect on basic dyes, and like bases in their effect on acidic dyes. E. G.

Catalysis. J. Leimdörfer (*Chem. Zentr.*, 1915, i, 419—420; from *Seifensieder-Zeit.*, 1914, **41**, 1253, 1275, 1297, 1323, 1345).—The basis of the author's hypothesis consists in the assumption of a new type between the atom or molecule and the visible crystal. By the aid of this "crystallom" an attempt is made to explain catalysis. Since chemical individuals are never in a perfectly homogeneous

state, it must be assumed that, in the narrowed sense of the world, all substances have crystalline character. Starting from the assumption that a heterogeneous condition is present in an actual gas, the author is led to the following definition: The actual condition of a gas is one of equilibrium characterised by the fact that those atoms present in the ideal state and with maximal energy content are in excess, whilst the liquid and solid portions with decreasing energy content are in the minority. Such a particle, in which all three states are present (solid, liquid, and gaseous), is the smallest individual which is perceptible to the senses. Since this is represented as the origin of crystals, the author has given the name "crystallom" to this smallest individual aggregate. Crystalloms are to be compared with the cells of the organised world.

With the help of this idea the author has depicted the phenomena of change of state and solution, the latter being defined as energy attraction between the crystalloms of the components of the solution.

Considerable analogy exists between the properties of solvents and catalysts. The latter are the sources of energy for the components of the reaction. The energy is imparted in the sense of the formula $A = C/R$ (A = chemical activity, C = available energy, R = space in which the quantity of energy is located). Catalysts, like solvents, after completion of catalysis (in the case of solvents, after separation of the compound formed from the solution) return to the original state of energy. The volume of a solid catalyst is greater than that which it would occupy in the liquid state, and hence it is to be assumed that the imparted energy is greater than that required for liquefaction. Since catalysts are regarded as very light, solid substances, it appears probable that this is a case of concentration of force, which is so located that the chemically active energy is greater than that exerted when the action is performed with the same substance in solution or in the liquid state. In such a finely divided substance, a condition exists which is characterised by a rapidly increasing aggregation of crystalloms. The normal condition prevails in the interior of the substance (for example, a metal functioning as catalyst), whilst at the surface the condition is comparable to the gaseous state. The transition from the interior to the surface of the little particles is very rapid; the external crystalloms are most highly charged with energy, the internal ones the least charged. The condition is similar to that obtained by the sudden liquefaction of a compressed gas. In addition to the distribution of forces thus depicted, the catalyst must also exist in a labile state, and be readily converted into the original form. A catalyst is therefore a substance with a high energy charge in a labile condition with respect to energy. All influences which diminish the charge or transform the substance into the stable state are catalyst poisons. H. W.

Promotion of Oxidations. Badische Anilin- & Soda-Fabrik (D.R.-P. 275518).—Very minute quantities of ruthenium or its

oxides or chlorides, or ruthenates are even more active catalysts of certain oxidations than other agents of the platinum group. The oxidation of hydrocarbons by air is an exception.

For example, ruthenium asbestos, prepared by mixing asbestos with an alkali ruthenate, causes the oxidation of methyl alcohol by air to formaldehyde at 120°, whereas a red heat is necessary in the case of platinum, palladium, or iridium. Phenanthrene, anthracene, and naphthalene are readily oxidised by boiling sodium chlorate solution acidified with acetic acid, if a trace of ruthenium chloride or potassium ruthenate is added. J. C. W.

The Activity of the Undissociated Molecule in Ester Catalysis. Eva Ramstedt (*Med. K. Vetens. Nobelinstitut*, 1915, **3**, [7], 1—33).—Measurements have been made of the rate of hydrolysis of ethyl acetate at 25° under the catalytic influence of β-naphthalenesulphonic, trichlorobutyric, cyanoacetic, and hypophosphorous acids. The concentration of the acid was varied, and in some experiments the rate of hydrolysis was determined in presence of the sodium salt of the catalysing acid. The degree of ionisation of the acids in the solutions was obtained from measurements of the electrical conductivity of the free acids and of their sodium salts over a considerable range of dilution.

It is found that the observed rate of hydrolysis can be represented by the equation $v = K_H c\alpha + K_M c(1-\alpha)$, in which K_H and K_M are coefficients characteristic of the hydrogen ion and of the unionised acid respectively, c is the concentration of the acid, and α the degree of ionisation. The agreement between the calculated and observed results applies to solutions containing both acid and the corresponding salt, as well as to solutions of the free acid. The value of the ratio K_M/K_H is for β-naphthalenesulphonic acid 0·98, for trichlorobutyric acid 0·055, for cyanoacetic acid 0·003, and for hypophosphorous acid 0·01.

On the assumption that the increase in the ionisation constant of acids with increasing concentration is due to the influence of the unionised molecules, it is shown that the greater this influence is, the greater will be the ratio K_M/K_H. By making use of this relation it is possible to anticipate the approximate magnitude of the ratio in the case of those acids which do not yield an ionisation constant. H. M. D.

Kinetics of Chemical Reactions. XI. E. I. Orlov (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 624—641).—The author has shown previously (A., 1913, ii, 938) that the formation of esters from organic acids and an alcohol in presence of a catalyst, or, in the case of formic acid, in presence of water alone, proceeds according to the equation:

$$dx/dt = k(A-x) - k_1 x \text{ or } dx/dt = k(A-mx).$$

The results of Kailan's investigations on the esterification of dibasic acids by means of alcoholic hydrogen chloride (A., 1914, ii, 41) give, for each experiment, a series of diminishing values of k, these being calculated from the equation:

$$0{\cdot}4343k = 1/t \,.\log [A/(A-mx)].$$

Like every ether-formation, the formation of an ester from an alcohol and a dibasic organic acid under the influence of a catalyst is a reaction of the first order, retarded in consequence of the liberation of water, which combines with part of the hydrogen ions of the catalyst to give the hydrate, $H_2O<\overset{H}{\underset{H}{}}$, so that the reaction extends over a long time. In presence of an initial quantity of water, A_1, the reaction will be expressed by the equation:

$$dx/dt = k(A-x) + k_1(A_1+x),$$

which, if $k - k_1 = mk$ and $QA = A + A_1(1-m)$, gives

$$dx/dt = k(QA - mx);$$

the constant mk for the last equation is calculated from

$$mk = 1/t \,.\, \log [A/(A - mx/Q)].$$

Now, the right-hand side of the latter represents the constant mk'/Q to the differential equation, $dx/dt = k'(A - mx/Q)$, and, as the integral of this, mk'/Q may be expressed thus:

$$mk'/Q = 1/t \,.\, \log [A/(A - mx/Q)].$$

Hence, $mk = mk'/Q$ or $k = k'/Q$. On these lines the velocity constants have been calculated from Kailan's numbers for the esterification of succinic, glutaric, tartaric, and oxalic acids. The formation of an ester from malic acid and an alcohol in presence of hydrochloric acid is more complicated than with these acids, three reactions taking place: (1) formation of the malic ester; (2) replacement of the hydroxyl group of the ester by a chlorine atom, $CO_2R{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2R + HCl \rightleftarrows CO_2R{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2R + H_2O$; (3) decomposition of the chlorosuccinic acid or ester into fumaric acid or ester and hydrogen chloride,

$$CO_2R{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2R \rightleftarrows CO_2R{\cdot}CH{:}CH{\cdot}CO_2R + HCl$$

(compare Müller, A., 1902, ii, 647). The differential equation corresponding with this complex process will be of the form $dx/dt = k(a-mx)/(C+mx)$, the numerator characterising the ester formation as a reaction of the first order, and the denominator indicating that reactions (2) and (3) are superposed on the ester-formation. The integral of this equation is:

$$mk = 1/t \,.\, [(a+C)2{\cdot}3 \log \{a/(a-mx)\} - mx].$$

The values of mk, calculated from Kailan's results, show a moderately high degree of constancy.

Nernst and Hohmann's data for the equilibrium between trichloroacetic acid and amylene (A., 1893, i, 449) show that this reaction also proceeds according to the equation:

$$dx/dt = k(a-mx)/(C+mx).$$

Zalkind and Pischtschikov's data for the velocity of hydrogenation of $\beta\epsilon$-dimethyl-$\Delta\gamma$-hexinene-$\beta\epsilon$-diol (this vol., ii, 435) also correspond with this equation, and calculation shows that, as long as not more than 60% of the glycol has reacted, the reaction proceeds with the mean velocity, 2·77, whereas after 60% has reacted, the velocity is 0·118; consequently, the process here comprises two stages, which at first take place together, so that the velocity of the first stage is $2{\cdot}77 - 0{\cdot}118 = 2{\cdot}652$, and that of the second, 0·118.

In the experiments of Nernst and Hohmann, and of Zalkind and Pischtschikov, C is not given by the experimental conditions, as is

the case in Müller's and in Kailan's investigations, but arises arbitrarily. This is explained by the appearance of intermediate forms between the reacting compounds, these directing the reactions in one direction or the other; it is possible to predict the character of these intermediate forms only by investigating the kinetics of the processes.

The results of Kailan's experiments on the hydrolysis of esters of dibasic organic acids under the influence of hydrochloric acid as catalyst are also considered. This hydrolysis proceeds according to the equation $dx/dt=k(e-x)+k_1(a_0+x)$, where e is the number of c.c. of barium hydroxide solution corresponding with the total acid formed by complete hydrolysis of the ester, a_0 the quantity of acid remaining in the ester, also expressed in c.c. of the barium hydroxide; x the quantity of ester which has reacted, expressed in c.c. of barium hydroxide, and k and k_1 constants. This equation may be put into the form $dx/dt=k(e'-mx)$, where $k-k_1=mk$ and $e'=e+a_0(1-m)$; the constants are calculated from the formula $0{\cdot}4343mk=1/t.\log[e'/(e'-mx)]$. In the case of ethyl malate, however, the reaction proceeds according to the equation:

$$dx/dt=k(e-x)+k_1(a_0+x)/(c+x),$$

where k and k_1 are constants, e is the acid-content of the ester, expressed in c.c. of barium hydroxide for complete hydrolysis; a_0 is the free organic acid of the ester, and c the content of hydrochloric acid, both being expressed in c.c. of barium hydroxide. This equation may be resolved into the form:

$$dx/dt=k(A-x)(B+x)/(c+x),$$

the constant being found by means of the formula:

$$k=1/t(A+B)[(A+c)\log\{A/(A-x)\}+(B+c)\log\{(B+x)/B\}.$$

T. H. P.

Atomic Structure. I. Changes of Mass and Weight Involved in the Formation of Complex Atoms. William D. Harkins and Ernest D. Wilson (*J. Amer. Chem. Soc.*, 1915, **37**, 1367—1383).—A theoretical paper in which it is shown that the relationships of the atomic weights of the elements render it very probable that the atoms are complex structures built up from hydrogen atoms. It is shown that the atomic weights of the twenty-six elements from helium to cobalt, although not integral multiples of the atomic weight of hydrogen, vary from the corresponding whole numbers by a nearly constant percentage difference of average value $-0{\cdot}77\%$. This percentage difference is termed the packing effect, and is regarded as representing the decrease of mass which would take place if the atoms were complexes built up from the hydrogen atom. This packing effect is remarkably regular, and explains the fact that the atomic weights on the oxygen basis are very nearly whole numbers; the variation of an atomic weight from a whole number on this basis indicates that the packing effect for this element does not have the average value. The probability that for the first twenty-seven elements, the sum of the deviations of the atomic weights (on the oxygen basis) from whole numbers should by accident be as small as it is, is only one in 15 million.

It is shown to be extremely probable that the electrons and positively charged particles which constitute the nucleus of a complex atom are packed exceedingly closely, and that consequently the electromagnetic fields of the charged particles must overlap to a considerable extent, whence it is evident that the mass of the atom should not be equal to the sum of the masses of the individual particles from which it is constructed. In order to give a decrease of mass equal to 0·77%, a positive and a negative electron would have to approach to a distance of 400 times the radius of the positive electron. This case does not correspond with any element actually known; the helium atom may be supposed to have a nucleus built up from four hydrogen nuclei and two negative electrons. E. G.

Atomic Structure. II. Structure of Complex Atoms. The Hydrogen–Helium System. WILLIAM D. HARKINS and ERNEST D. WILSON (*J. Amer. Chem. Soc.*, 1915, **37**, 1383—1396. Compare preceding abstract).—In this paper it is shown that the system which has been found to apply to the atomic weight and valency relations of the members of each of the radioactive series also holds true for the lighter atoms. In a radioactive series it is found that the loss of an α-particle with a mass of four decreases the valency by two, and thus shifts the elements two groups to the left in the periodic table and decreases the atomic number by two. If this were true for the lighter elements, beginning with helium, the addition of the weight of a helium atom for each increase of 2 in the atomic number ought to give the atomic weights of the elements belonging to the even-numbered groups. The atomic weights thus obtained agree with the recorded values, the theory thus being in harmony with the facts.

In the preceding paper it has been shown that the magnitude of the packing effect for helium is 0·77%, which is the same as the average of the packing effects for the first twenty-seven elements; if, then, a more complex atom is constructed of helium groups alone, nearly all the packing effect is, in general, due to the primary formation of the helium nucleus from four hydrogen nuclei and two negative electrons, and scarcely any packing effect results from the aggregation of these helium nuclei into more complex atoms. According to this view, the helium nuclei must be so much more stable than the nuclei of the more complex atoms which they form that an atom made up entirely from helium units should give helium, and not hydrogen, by its primary decomposition. This is in accord with the behaviour of the radioactive elements when they disintegrate. E. G.

Atomic Structure. III. Recent Work on the Structure of the Atom. WILLIAM D. HARKINS and ERNEST D. WILSON (*J. Amer. Chem. Soc.*, 1915, **37**, 1396—1421).—All the more important recent work on the complexity of atomic structure is reviewed, and a bibliography is appended. E. G.

Graphic Representation of the Relation between Atomic Weights and the Velocity of Movement of the Atoms of Elements at their Melting Points: Direct Conclusions concerning the Natural System of the Elements. P. P. von Weimarn (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 481—489. Compare this vol., ii, 411).—The author has constructed three curves, each of which has the atomic weights of the elements as abscissæ, the ordinates being the absolute melting point T_s, T_s/A, and $\sqrt{T_s/A}$ respectively. The greatest regularities are shown by the last two of these curves, and especially by the third, the ordinates of which are proportional to the intensity factors of the energy of atomic motion at the melting points. Either of these two curves exhibits small and large periods, the structures of all the corresponding periods being similar. The large periods show, in addition to the principal periods, also secondary ones, so that principal and secondary maxima and minima are present. The points occupying the principal maximum positions lying on the flat ridges of the principal periods are occupied by similar elements, for instance, vanadium, chromium, manganese, iron, cobalt, and nickel, or columbium, molybdenum, ruthenium, rhodium, and palladium. At the ridges of the secondary periods are found germanium and arsenic; tin and antimony; thallium, lead, and bismuth; the minima of the secondary periods are occupied by gallium, indium, and mercury, which melt readily, are to a marked extent "noble," and exhibit variable valency (compare Biltz, *Zeitsch. Elektrochem.*, 1911, **17**, 670). The broken lines connecting the different groups of elements are highly characteristic, and follow similar courses; if nitrogen, oxygen, and fluorine are excluded, all these lines fall as the atomic weight increases.

The curves lead to interesting conclusions concerning the position of hydrogen in the natural system of the elements. Ramsay, among others, considers that this element is to be regarded as the first member of the halogen group, and Biltz (*loc. cit.*) states that a study of his curve renders such a position for hydrogen inevitable. The possibility that other elements may yet be found between hydrogen and helium cannot, however, be overlooked. From the value of $\sqrt{T_s/A}$ for hydrogen and the position of the latter on the curve, this element approaches those capable of existing under ordinary conditions in both the metallic and non-metallic states.

If the values of A and T_s are known and the position of the element in the periodic system, it is possible to determine the magnitudes of many properties of the element at the melting point, and also, if the temperature-coefficients of these properties are known, at any other temperature. T. H. P.

Numerical Relationships between Electronic and Atomic Constants. H. Stanley Allen (*Proc. Physical Soc.*, London, 1915, **27**, 425—431).—According to Jeans, the quantity hc, where h is the constant involved in the quantum theory, and c the velocity of light, has the same dimensions as the square of an electric charge. The relation between h and the charge e of the electron may be

written in the form $4\pi^2e^4/h^2c^2 = p = 5{\cdot}30096 \times 10^{-5}$. It is shown that several of the fundamental physical constants, expressed in the usual electrostatic units, contain simple multiples of the number p. The charge on an electron is within 0·1% equal to $9p \times 10^{-6}$. The ratio e/m of the charge to the mass is equal to $p \times 10^{22}$ and $m = 9 \times 10^{-28}$. By accepting these values for e and m together with $c = 3 \times 10^{10}$, it is shown that derived quantities can be expressed in terms of simple integers (2, 3, or 4), powers of 10, p, and π. The coincidences suggest the possibility of some accidental connexion between the units of length, mass, and time involving the number 10. H. M. D.

Modern Development of Stereochemistry. M. Scholtz (*Ber. Deut. pharm. Ges.*, 1915, **25**, 225—255).—A lecture summarising our present knowledge of stereochemistry due to asymmetric atoms of elements other than carbon. D. F. T.

Some Aspects of the Theory of Acids. Arthur Lapworth (T., 1915, **107**, 857—868).—A theoretical paper dealing with the functions of ionised and non-ionised acids, and the changes in the activity of acids in different media. The action of the hydrogen ion and the non-ionised acid is discussed from considerations of their thermodynamic potentials. An interpretation of the anti-catalytic action of water on alcoholic hydrogen chloride is given, which is based on the solvation of the ions. J. F. S.

The Valency Volume Theory. Thomas Vipond Barker (T., 1915, **107**, 744—773).—A criticism of the fundamental conceptions underlying the Barlow-Pope theory, and of the methods employed in its crystallographic application.

In connexion with the derivation of the law of valency volumes, it is pointed out that a strict adherence to close-packed systems of initially spherical atomic components implies a very serious limitation of the available number of structural types. In the cubic system, for example, it involves the exclusion of two out of the three simple space-lattices. The author holds that there is no justification for such invidious selection, and that Barlow and Pope's description of the processes involved in the actual deduction of the law of valency volumes from the principle of close-packing is too incomplete to admit of an adequately close examination.

The methods employed by the adherents of the theory in their appeal to the quantitative data of crystallography are examined, and it is pointed out that the illustrative sphere assemblages, which have been designed with a view to a close correspondence with the axial ratios of a crystal, cannot always be held to be, even approximately, exact reconstructions, inasmuch as the initial correspondences can scarcely survive the subsequent elimination of interstitial space during the transformation of the system of spheres plus cavities into a space-filling system of plane polyhedral cells. The introduction of "equivalence parameters," so far from having served any purpose for which axial ratios are unfitted, has led the adherents of the theory to undertake a large amount of computa-

tive work, which has no crystallographic value, whether the theory be correct or not.

From a discussion of the purely arithmetical verifications of the theory, which involve such arbitrary selections of the axial ratios as would never be suggested by the geometrical development of the crystal, it is shown that the methods followed by Barlow and Pope can be made to yield any desired numerical result—in some cases in several different ways.

Reference is made to the chondrodite series of minerals, and to certain derivatives of camphor as being typical examples of substances which have been held by the adherents of the theory to furnish collateral quantitative evidence in its support. The author believes the axial ratios suggested by Penfield for the chondrodite minerals to be unsatisfactory in the sense that they are a very cumbrous reflexion of the analytical data. On the other hand, the complex form development is in agreement with the simpler view that we are dealing with a series of isomorphous mixtures, characterised by slightly fluctuating axial ratios instead of the progressive increments involved in Penfield's interpretation. In regard to the camphor derivatives, it is shown that these afford typical examples of the ambiguity which attaches to the ordinary goniometrical data. Until such ambiguity can be eliminated, it will not be possible to confirm or disprove the valency volume theory by appeals to quantitative crystallographic data.

In the third section, the author discusses the problems which have to be solved before reliable deductions relative to molecular structure can be made from goniometrical data. The Bravais principle is advocated as the only trustworthy guide in deducing the space-lattice constants, and it is shown that the material used by Barlow and Pope fails to withstand this objective method of criticising the form development of individual crystals. The question of the comparison of two or more crystals, or of a crystal with its model, is also dealt with, and this is followed by a detailed discussion of every individual case which the author holds to be relatively cogent. It is found that the whole of the material advanced by the adherents of the theory contains only five substances in which the treatment of the geometrical evidence is in accordance with objective methods of criticism, and the author draws the conclusion that the valency volume theory has so far received no general support from crystallographic data. H. M. D.

Electron Conception of Valence. VII. Theory of Electrolytic Dissociation and Chemical Action. K. George Falk and J. M. Nelson (*J. Amer. Chem. Soc.*, 1915, **37**, 1732—1748).—In this paper the relation between the changes occurring in chemical reactions and the degree of electrolytic dissociation of one or more of the reacting substances is discussed in the light of the electron conception of valence (A., 1911, ii, 104, 171; 1913, ii, 768; 1914, ii, 44, 193; this vol., ii, 95), and the following conclusions are drawn. The changes occurring in chemical reactions need not be considered to depend on electrolytic dissociation of the reacting

substances. Every chemical reaction is a reaction between charged atoms, ions being merely a special case of charged atoms. Certain properties of a solvent render some of these charges evident to experimental methods, whilst other, or perhaps often the same, properties increase the extent or rate of a reaction. E. G.

Valency of the Elements and Complex Compounds. G. Povarnin (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 217—262, 501—528). —The first paper consists of a criticism of Werner's co-ordination theory and of an attempt to replace it, particularly as regards the arbitrary assumption of complementary valencies. It is urged against this theory that: (1) it assumes the existence of three types of valencies; (2) it makes a distinction between atomic and molecular compounds; (3) it contradicts the significance of the periodic law for the numbers of the complementary valencies and of the two kinds of principal valencies; (4) in many cases it is difficult to prophesy with its aid. As an example, the following compounds are considered: $[Co(H_2O)_6]Cl_2=CoCl_2,6H_2O$;

$[Co(H_2O)_6]Cl_3=CoCl_3,6H_2O$;

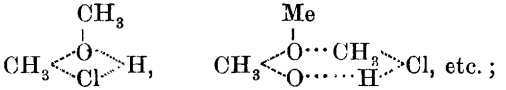
$[Pt(NH_3)_6]Cl_4$; $[Pt(Cl)_6]M_2$. These schemes do not explain the connexion between the internal and external spheres, and, further, they combine under one co-ordination number derivatives of cobaltous and cobaltic oxides; the number of atoms in the external sphere of the plato-compounds cannot be foreseen, and must be determined empirically.

The foundation of the author's theory is the possession by the atom of positive and negative charges, the relative magnitudes of these depending on the structure of the atom; there is no basis for the supposition that the absolute magnitudes of the negative charges are invariably the same as those of the positive charges. Thus, the classical unit of valency is regarded as composed of two polar charges, not identical in absolute magnitude. It is considered that the linkings exhibit a more or less marked ability to oscillate, and that there is a tendency for the atoms to form four- or six-membered cyclic molecules.

On these lines the author develops the structures of complexes of some of the principal types, especially those in which the groups H_2O, NH_3, and NO_2 occur.

In the second part of the paper, structures are given for the various types of complex containing platinum, cuprammonium complexes, biuret complexes, thio-complexes, aluminosilicates, etc.

The theory of polar affinities is considered also in its relation to: the oscillation hypothesis; ring formation; the tervalency of carbon; the structure of oxonium derivatives, the compounds of hydrogen chloride with methyl ether, for example, being represented thus:



chromo-isomerism, etc. T. H. P.

A Simple Instrument for the Determination of Viscosity. ALAN SPEEDY (*J. Soc. Chem. Ind.*, 1915, **34**, 597—598).—A piece of glass-tubing about 20 cm. long is drawn out in the middle to a capillary about 6 cm. long, and bent into a narrow U-tube. About 8 cm. from the bend the limbs are marked with levels, *aa'*, and one limb is provided with another mark *c* nearly 1 cm. above *a*, and a third mark, *b*, about 2·5 cm. above *c*. The instrument is fixed in the thermostat, or strapped to a thermometer, in a bath, so that *aa'* are just above the surface of the heating liquid. The liquid to be examined is filled up to *aa'* and, when the conditions are adjusted, the liquid is sucked up to *b* and the time taken to fall to *c* is recorded. The instrument is calibrated with phenol or sulphuric acid.

The advantages of this simple appliance are that only a small bath is required, and the heating liquid need not be transparent. It gives sufficiently accurate results. J. C. W.

Collodion Membranes for Ultrafiltration and Pressure Dialysis. GEORGE STANLEY WALPOLE (*Biochem. J.*, 1915, **9**, 284—297).—The membranes described are in test-tube form, or, better, flat films, made by pouring alcohol–ether solutions of collodion on to bevelled plate glass; the membrane after evaporation of the solvent is then plunged into water. Very uniform results are obtained. Their permeability to simple molecules and water is high, and filtration through them is rapid. They retain quantitatively all antigens. It is suggested that the channels through the gel structure are of uniform size, but that they are small and numerous. W. D. H.

The Bicycle Ergometer. AUGUST KROGH (*Proc. Physiol. Soc.*, 1915; *J. Physiol.*, **49**, xxxi—xxxii).—This instrument has been tested with good results in Benedict's calorimeter; its special feature is an automatic device (figured) for regulating the work per revolution. W. D. H.

Apparatus for Carrying Over by means of a Gas the Vapours Emitted by a Substance. E. MAUGUIN (*Rev. gen. Chim. pure appl.*, 1914, **17**, 196).—A description of a simple apparatus by means of which there can be obtained a mixture of vapour from a compound and a gas at any given temperature and at a uniform rate. It consists essentially of a glass cylinder sealed inside another glass cylinder, each cylinder being furnished with inlet and outlet tubes. The outer cylinder acts as a constant-temperature bath, and is filled with a suitable liquid. The inner cylinder contains the substance to be vaporised, and the gas is passed into it at one end, the mixture of gas and vapour issuing from the other end being passed to the reaction vessel. This apparatus is very useful as a source of gas–vapour mixture in Sabatier's catalytic processes, and is sketched in the original. W. G.

Gas-washing Apparatus with Enclosed Filter. E. R. WEAVER and J. D. EDWARDS (*J. Ind. Eng. Chem.*, 1915, **7**, 534—535).—The

apparatus is of the type described by Cumming (A., 1910, ii, 841), the gas being admitted into an inclined tube connected with a reservoir, so that the bubbles of gas passing along the tube cause the liquid to circulate. The inclined tube may have a corrugated upper surface to prolong the contact of the gas with the liquid, and the liquid reservoir may consist of a cylinder provided with a tap; a filter is placed above the tap to collect any precipitate which may form, the tap being opened at the end of the absorption period and the liquid allowed to flow through the filter. In another form of the apparatus, the tube in which the gas is washed is arranged as a helix round a cylindrical reservoir, the latter being provided with a filter and tap. W. P. S.

Apparatus for the Absorption and Recovery of Gases. E. Mauguin (*Rev. gen. Chim. pure appl.*, 1914, **17**, 196—198).—A description of a simple apparatus for the absorption of gases by suitable liquids, in which the gas is for a long time in contact with a large surface and big volume of reagent. Once the apparatus is charged and regulated, it can be worked for several days without being touched. The absorbing reagent can easily be collected, and thus the gas regenerated. The apparatus is sketched in the original. W. G.

Automatic Filter Washer. J. M. Pickel (*Chem. News*, 1915, **112**, 3—5).—The apparatus consists of a long, rectangular tank divided into a number of compartments, each holding about 250 c.c. of water; an overflow at one end of the tank enables all the compartments to be filled at the same time. Each compartment is fitted as follows: A T-piece is soldered into the bottom of the compartment; the side-branch of this T-piece carries a water-gauge, whilst the vertical branch is attached to a tapped glass tube containing a small siphon. The rate of flow of water from the compartment to the tube is regulated by turning the tap, and the siphon delivers the water intermittingly into a funnel placed beneath and containing the filter, etc., to be washed. W. P. S.

Device for Obviating the Kinking of Rubber Tubing Connexions of Water-jacketed Condensers. A. Cottrell and H. Wright (*Chem. News*, 1915, **112**, 3).—A length of brass wire is wound spirally round the tubing at the place where the latter is liable to kink, and the tubing is then bent to a suitable curve. W. P. S.

Inorganic Chemistry.

A Chlorine Generator. A. Vosmaer (*Chem. Weekblad*, 1915, **12**, 576—577).—The apparatus consists of a two-necked Woulfe's bottle containing a layer of glass marbles at the bottom, and over this granulated manganese dioxide. The acid reservoir is placed about

50 cm. higher than this bottle, and the acid is added slowly, the manganese dioxide being maintained at about 50°. Provision is also made for tapping off the waste acid. The generation of chlorine can be continued without interruption for a long time.
A. J. W.

Temperature at which Hydrogen Chloride is Evolved during the Evaporation of Magnesium Chloride Solution. H. Hof (*Chem. Zeit.*, 1915, **39**, 470).—When magnesium chloride solution is heated in a flask by means of an oil-bath, practically the whole of the water may be evaporated without loss of hydrogen chloride, provided that the level of the surface of the oil is below that of the solution. The vapours begin to contain hydrogen chloride when the temperature of the solution reaches 157°, the boiling point of magnesium chloride hexahydrate. If the level of the oil is above the level of the solution in the flask, hydrogen chloride may be detected in the escaping vapour when the temperature of the solution rises to 107°, but this is due to the side of the flask above the solution being overheated. W. P. S.

Hydrolytic Reactions which take place when Waters are Evaporated and the Residues Dried and Ignited. P. Kaschinki (*Chem. Zentr.*, 1914, ii, 893; from *J. Russ. exper. Landw.*, 1913, 368—375).—When a highly saline water is evaporated and the residue ignited, considerable loss of chlorine, bromine, and iodine takes place; about 25% of the chlorine present may be expelled during the evaporation, and the loss is increased to 50% when the residue is heated at 180°. Loss of sulphuric acid also takes place. The weight of the solids obtained on evaporating the water varies with the conditions under which the latter is evaporated (size of the basin, etc.) (compare also A., 1913, ii, 974). W. P. S.

Preparation of Sodium Hypochlorite. Mario Ricci (*Ann. Chim. Applicata*, 1915, **3**, 282—284).—Severe criticism of Cattaria and Ranucci's results (this vol., ii, 344). T. H. P.

Factors Influencing the Stability of Hypochlorite Solutions Martin L. Griffin and John Hedallen (*J. Soc. Chem. Ind.*, 1915, **34**, 530—533).—Experiments have been conducted in order to learn the influence of various factors on the stability of calcium hypochlorite solutions. The work depended on the accurate estimation of "total chlorine" and "available chlorine," and the existing methods were therefore tested. Bunsen's method, whereby the bleach liquor is added to excess of potassium iodide, acidified by acetic acid, and the liberated iodine is titrated, is preferred for the latter purpose. The analysis of a mixture of hypochlorite, chloride, and chlorate as described in Sutton's "Volumetric Analysis," is found to be expeditious and trustworthy, but as only the amount of "total chlorine" is required in routine analyses, the process may be modified as follows: 5 c.c. of the liquor are measured into a pressure flask, mixed with about 25 c.c. of 4% ferrous ammonium

sulphate solution and 40 c.c. of sulphuric acid, heated at about 100°, and precipitated with excess of silver nitrate, and after filtering, the excess of silver is titrated.

Small quantities of calcium hypochlorite solution are stable if they contain 5% of free calcium hydroxide. On the large scale, however, larger excesses of lime must be employed, and even an excess of 25—30% is ordinarily used. The excess separates as "lime sludge," and the availability of this in further preparations has been made the subject of experiment. It is found that, keeping the excess of calcium hydroxide at 10%, the sludge can only be used again to give stable hypochlorite solutions if it is mixed with at least three times as much fresh lime. If, however, the excess of calcium hydroxide is about 80%, then the sludge itself can be used without fresh lime.

A further series of experiments dealt with the common impurities in lime. The influence of aluminium hydroxide depends on the protection afforded by the excess of lime. With an excess of 13%, stable solutions are obtained even if 10 grams per litre of aluminium hydroxide are present. Ferric hydroxide, however, very rapidly spoils the solutions. Magnesium hydroxide has no effect if at least an excess of 5% of lime is present, but cannot replace the lime. If the lime is exhausted, not even large excesses of magnesium hydroxide will preserve the solutions. When chlorine is passed into a suspension of calcium and magnesium hydroxides, none of the latter will dissolve until all the lime has reacted.

Concentration and temperature have little influence on the stability of calcium hypochlorite solutions. J. C. W.

Preparation of Salts of Complex Hydrofluoric Acids. Gebrüder Siemens & Co. (D.R.-P. 279011).—Borofluorides titanifluorides, or silicofluorides, and the like are prepared by adding hydrofluoric acid to a mixture of the oxy-compound of the other constituent of the complex acid radicle (boric acid, titanic acid, or silicic acid) with the oxide or a salt of a metal, in the quantities calculated for the final salt. Thus, boric acid and potassium chloride are stirred into a thin paste with water, and hydrofluoric acid is added, when an almost quantitative yield of potassium borofluoride is obtained at once. The sodium salts are much more soluble than the potassium salts, and are, therefore, rather difficult to purify. J. C. W.

Experiments on the Distillation of Liquid Air in a Magnetic Field. R. S. McBride (*J. Amer. Chem. Soc.*, 1915, **37**, 1715—1718).—The experiments described in this paper were carried out in view of a suggestion that the magnetic properties of liquid oxygen might render it possible to improve the separation of oxygen and nitrogen by distilling liquid air in a strong magnetic field. The results indicated that the rate of evaporation was about 5—10% greater in the magnetic field, and that more oxygen was volatilised during the early part of the distillation in the magnetic field than in a similar distillation outside the magnetic field. It seems,

therefore, that the magnetic field exerts a beneficial influence on the separation, but the experiments were too few to afford conclusive proof. E. G.

Method for Increasing the Stability of Hydrogen Peroxide in Neutral, Liquid or Solid Carriers. E. MERCK (D.R.-P. 275499).—The stability of solutions of hydrogen peroxide or of its solid compounds with carbamide, ammonium sulphate, etc., can be increased enormously, without rendering the mixture acid, by the addition of acyl derivatives of aminohydroxycarboxylic acids. Examples: (1) β-Dimethylamino-α-benzoyloxy*iso*butyric acid, $NMe_2 \cdot CH_2 \cdot CMe(OBz) \cdot CO_2H$, is added to 1000 parts of acid-free 3—30% hydrogen peroxide. (2) Carbamide (600 parts), 15% pure hydrogen peroxide solution (2500) and 1 part of benzoylecgonine, are evaporated in a high vacuum. (3) Powdered ammonium sulphate (60) and 30% hydrogen peroxide (75) are mixed and cooled, shaken with α-benzoyl-β-piperidinopropionic acid (0·05), and dried in a vacuum. J. C. W.

Rhythmic Phenomena in the Solidification of Sulphur. ALBRECHT VON FISCHER-TREUENFELD (*Kolloid. Zeitsch.*, 1915, **16**, 109—111).—The author describes ring and dendritic structures which have been observed when thin films of liquid sulphur are allowed to crystallise. The effects are ascribed to the action of capillary forces, in virtue of which the crystalline aggregates exert an attractive force on the neighbouring liquid. H. M. D.

Oxidation of Hydrogen Sulphide by Bacteria. H. C. JACOBSEN (*Chem. Zentr.*, 1915, i, 324—325; from *Folia mikrobiol. Holländ Beitr. gesamt. Mikrobiol.*, 1914, **3**).—Hydrogen sulphide is oxidised by the sulphur bacteria and by the thiobacteria described by the author. This can be readily demonstrated by adding 1—2 mg. of hydrogen sulphide to a culture solution placed in an Erlenmeyer flask provided with a rubber stopper carrying a funnel and bent glass tube. After one to two days the odour of hydrogen sulphide has entirely disappeared; in the film of bacteria a large variety of the latter is found, together with numerous minute globules of sulphur, which, however, are not deposited within the cells. When the film of bacteria has been formed, the amount of hydrogen sulphide can be increased, and further oxidation proceeds briskly. The second phase of the process, the oxidation to sulphuric acid, requires a much longer time. The film of bacteria fulfils the function of oxygen-carrier during the oxidation of hydrogen sulphide to sulphur; the bacteria which are chiefly found in the crude cultures belong to the type *Thiobacillus thioparus*.

By means of special experiments it is shown that the oxidation of hydrogen sulphide to sulphuric acid proceeds quantitatively, and that the substance of the bacteria is formed by reduction of carbon dioxide. In the second phase of the oxidation the thiobacteria are autotrophically nourished. H. W.

Formation of Free Sulphuric Acid from Sulphur. W. ZÄNKER and E. FÄRBER (*Chem. Zentr.*, 1914, ii, 1219—1220).—Sulphur in the free state or loosely combined on cotton-wool can be converted into sulphuric acid either by itself or by the aid of a contact substance, such as the porous fibres. The authors have attempted to determine whether sulphuric acid is formed in appreciable amount from sulphur when the latter is fixed to the cellulose fibre by a process similar to that which occurs in dyeing.

The slight sulphuric acid content of different varieties of sulphur does not appear to be generally recognised. Its presence in roll sulphur can only be detected by special means, which are described in the original. Powdered sulphur from different sources cannot be completely freed from acid by repeated washing, and it therefore appears probable that the latter is continuously formed by the action of air and moisture during the process. Flowers of sulphur contain the greatest amount of free sulphuric acid, roll sulphur much less; colloidal sulphur remains almost as strongly acid after washing as washed flowers of sulphur.

In order to confirm the assumption that the formation of free sulphuric acid from fixed sulphur in the presence of air and moisture is facilitated by contact action of the cellulose fibre, the larger surface exposed and the finer state of division, cotton yarn has been impregnated with sulphur in neutral solution; after being dried and allowed to remain for some time, the yarn is invariably found to have an acid reaction. The mode of fixation of sulphur on the cotton has an appreciable effect, but the quantity appears to be of greater importance.

The formation of free sulphuric acid from flowers of sulphur or powdered sulphur is most readily demonstrated by washing a quantity of the finely divided material with cold and with hot water, treatment with a little ammonia, and subsequent washing until the water has a neutral reaction; the product is covered with water at 60—80°, and repeatedly dried and re-moistened. Formation of acid is facilitated by passing a current of air. The autoxidation of sulphur occurs more readily in an acid than in a neutral or alkaline medium.

The authors apply their results to the processes of decomposition of sulphur-blacks. The most striking similarity lies in the fact that formation of acid proceeds rapidly when traces have been formed. The instability of many sulphur-blacks is to be attributed to the presence of free or readily liberated sulphur. The total amount of acid formed from these dyes, however, is not due to free sulphur; the dye itself participates in the formation of acid.

H. W.

Reducing Properties of Hyposulphurous Acid. I. Action of Sodium Hyposulphite on Selenium and Tellurium. L. A. TSCHUGAEV and V. G. CHLOPIN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 364—372).—When heated with an alkaline solution of sodium hyposulphite in absence of air, tellurium is converted into the unstable sodium telluride, Na_2Te, sodium sulphide being also

formed. The tellurium is probably first transformed by the sodium hydroxide into a mixture of sodium tellurite and telluride, the latter being then converted by the tellurium into polytellurides, which undergo reduction by the sodium hyposulphite:

$$Na_2S_2O_4 + Na_2Te_2 + 4NaOH = 2Na_2SO_3 + 2Na_2Te + 2H_2O.$$

This reduction is analogous to the action of the hyposulphite on sodium polysulphides (compare Binz, A., 1905, ii, 521). It is possible that the tellurium combines with the sulphoxylate part of the hyposulphite molecule, $Na{\cdot}SO{\cdot}ONa + Te = Na{\cdot}Te{\cdot}SO{\cdot}ONa$, the unstable compound thus obtained reacting with the sodium hydroxide, thus:

$$Na{\cdot}Te{\cdot}SO{\cdot}ONa + 2NaOH = Na_2Te + O{:}S(ONa)_2 + H_2O.$$

The formation of the sodium sulphide also obtained in the reaction is probably explained by the equations:

$$2Na_2S_2O_4 + 2NaOH = Na_2S_2O_3 + 2Na_2SO_3 + H_2O,$$

and $$Na_2S_2O_3 + Na_2S_2O_4 + 4NaOH = Na_2S + 3Na_2SO_3 + 2H_2O.$$

The extreme instability of sodium hyposulphite makes it difficult to prepare sodium telluride in large quantities in the above manner. A good yield may, however, be obtained by heating, in a current of hydrogen, a mixture of tellurium (1 gram), sodium formaldehydesulphoxylate (rongalite) (6 grams), and 10% sodium hydroxide solution (40 c.c.):

$$OH{\cdot}CH_2{\cdot}O{\cdot}SONa + Te + 2NaOH = CH_2O + Na_2Te + Na_2SO_3 + H_2O.$$

Sodium telluride is instantaneously decomposed in the air, with separation of tellurium.

Benzyl telluride, $Te(CH_2Ph)_2$, obtained from a solution of sodium telluride with either the calculated quantity of benzyl chloride or a solution of phenylbenzyldimethylammonium chloride, forms pale yellow needles, m. p. 53—53·5°.

Selenium behaves towards sodium hyposulphite or rongalite in the same way as tellurium, yielding sodium selenide, which may be converted into benzyl selenide, m. p. 45°. In similar conditions sulphur dissolves only slightly in an alkaline solution of hyposulphite or rongalite.

The reaction between sodium hyposulphite or rongalite and a small quantity of tellurium or selenium in a sealed tube proceeds very rapidly and smoothly, and serves as a lecture experiment to demonstrate the preparation of sodium telluride or selenide.

T. H. P.

Compounds of Selenium with Silver. Giovanni Pellini (*Gazzetta*, 1915, **45**, i, 533—539).—The melting-point diagram of the system silver–selenium rises rapidly from the melting point of selenium, 217°, to 616°, and then remains horizontal between 4—5 and 52 atom. % of silver, beyond which it again rises rapidly to a maximum of 897°, corresponding with 66·6 atom. % Ag. Next a sharp fall takes place to 845° (67—68 atom. % Ag), this being followed by a rise to 890°, at which point the temperature remains from 68 to 89 atom. % Ag. Finally a rise occurs to the melting point of silver. The melting point found for the compound Ag_2Se, 897°, is higher than the values given by Pélabon (A., 1906, ii, 667;

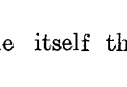
1909, ii, 805) and Friedrich and Leroux (A., 1908, ii, 696), namely, 880° and 850° respectively. Like the analogous compounds, Ag_2S, m. p. 842° (Jaeger and Klooster, A., 1912, ii, 1170), and Ag_2Te, m. p. 959° (Pellini and Quercigh, A., 1910, ii, 1063), Ag_2Se melts without decomposition. No compound analogous to AgTe is formed in the case of selenium. The three compounds, Ag_2S, Ag_2Se, and Ag_2Te are polymorphous-enantiotropic, the transformation points being at 90° and 179°, 122° and 138° respectively. Silver selenide exhibits miscibility gaps in the liquid state with silver and selenium, just as is found with the system Sb–S (Jaeger and Klooster, *loc. cit.*), and, possibly, Sn–Se (Guertler, "Metallographie," I., 966). The tellurides of silver present no miscibility gaps with their respective components, but silver shows such a gap with Ag_2S, study of mixtures richer in sulphur not being possible. T. H. P.

Course of the Oxidation of Nitrogen in Electric Discharge in Presence of Ozone. II. Viktor Ehrlich and Franz Russ (*Monatsh.*, 1915, **36**, 317—354. Compare A., 1912, ii, 41).—The observations described in the previous paper have been extended in order to ascertain the connexion between the chemical changes which take place during the discharge and the electrical conditions. The results obtained show the existence of a close relation between the discharge potential and the chemical composition of the gaseous mixture. In particular it has been found that the presence of small quantities of ozone and nitrogen pentoxide increases the discharge potential. The formation of these substances consequently gives rise to considerable changes in the nature of the electrical discharge. H. M. D.

Oxygenated Compounds of Nitrogen. II. Constitution of Nitrogen Peroxide and the Products it forms with Limited Proportions of Water. Giuseppe Oddo (*Gazzetta*, 1915, **45**, i, 413—443. Compare Oddo and Cesaris, A., 1914, i, 1174).—The author first discusses various structures which have been suggested for nitrogen peroxide and certain of its derivatives. When completely dried by means of phosphoric oxide and purified by distillation and crystallisation, nitrogen peroxide forms a limpid, red liquid, b. p. 22—23°, solidifying at −9·04°.

Its cryoscopic behaviour in various solvents has been investigated. In nitrobenzene, it dissolves almost entirely in the form of simple molecules, but in benzene, it shows a marked tendency to polymerise with increase of the concentration. In acetic acid, it tends to dissociate into $2NO_2$, the molecular weights being always less than the normal, which is, however, approached more and more nearly as the concentration increases. This variation in behaviour depends largely on the temperature of solidification, but a part is also played by the nature of the solvent.

In solution in nitrobenzene, water forms simple molecules at low concentrations, and yields rather higher molecular weights at slightly higher concentrations. On the other hand, in solutions of nitrogen peroxide in nitrobenzene, water gives values for the

molecular weight which at small concentrations approach, and subsequently exceed, three times the theoretical number. In these conditions there is, therefore, a tendency to form a hydrate of nitrogen peroxide, and for this the name nitrosic acid is suggested; to this acid the structure $O{:}N(OH)\langle{}^{O}_{O}\rangle N{\cdot}OH$ is attributed, and to nitrogen peroxide itself the formula  . Thus, nitrosic acid results from the addition of 1 mol. of nitric acid to 1 mol. of nitrous acid, and the fact that the somewhat basic function of the $:N{\cdot}OH$ group tends to reconvert it, by way of the ammonium salt, into the anhydride, explains its instability. Nitrogen peroxide may, therefore, be regarded as nitrosic anhydride.

The formation of nitrosic acid is supported by the behaviour of water in benzene or acetic acid solutions of nitrogen peroxide, and by that of alcohol in benzene solutions of the peroxide. The organic nitrosates, furnished by the action of nitrogen peroxide on ethylenic compounds, are to be regarded as derivatives of nitrosic acid, and the acid salts, KNO_3,HNO_3 and $KNO_3,2HNO_3$, as monopotassium salts of dinitric acid, $OH{\cdot}NO\langle{}^{O}_{O}\rangle NO{\cdot}OH$, and trinitric acid, $OH{\cdot}NO\langle{}^{O}_{O}\rangle N(OH)\langle{}^{O}_{O}\rangle NO{\cdot}OH$, respectively.

It appears, then, that the higher oxygenated compounds of nitrogen exhibit a certain tendency to form complexes by polymerisation. Unlike those furnished by sulphur (compare Oddo and Anelli, A., 1911, ii, 717), phosphorus, and silicon, these compounds dissolve very readily into the simple component molecules, and thus constitute highly sensitive, reversible systems. T. H. P.

Explosibility of Mixtures of Air and Ammonia. E. Schlumberger and W. Piotrowski (*Chem. Zentr.*, 1914, ii, 1421).—Mixtures of air and ammonia of definite composition are explosible. Under the experimental conditions adopted by the authors with regard to size and shape of vessel, ignition, and humidity, the region of explosibility lies between 16·5 and 26·8% NH_3 by volume. In the Bunte burette an actual explosion is not observed, progressive combustion taking place between the limits 19—25% NH_3. The stoicheiometric mixture is 21·9% NH_3 by volume. H. W.

Preparation of Boric Acid Compounds [Pertetraborates] Containing Active Oxygen. J. Auer (D.R.-P. 281134; from *J. Soc. Chem. Ind.*, 1915, **34**, 613).—Pertetraboric acid or its salts, for example, the *sodium* salt, $Na_2B_4O_{11}$, are prepared by the action of hydrogen peroxide, or a mixture with a metallic peroxide, on pyroboric acid, preferably at below 0°. J. C. W.

The Anodic Behaviour of Alkaline Borate and Perborate Solutions. Wilfrid Gustav Polack (*Trans. Faraday Soc.*, 1915, **10**, 177—196).—The effect of electrolysing solutions of sodium and

potassium borates, with varying proportions of alkali hydroxide, has been examined in detail. The anode is a narrow platinum tube, and the cathode, which is placed in the outer space, is of sheet nickel. The diaphragm is of asbestos paper, or a porcelain cell reduced in thickness by turning. A cooling liquid circulates through the anode and through a glass spiral in the anode space. The anode liquid is also caused to circulate. Perborate is not formed, even when the anode is thoroughly cooled, and even very concentrated solutions only yield a minute quantity. Perborates introduced into the anode solution are destroyed, owing to the formation of hydrogen peroxide. This has been confirmed by measurements of the anode potential. The results are in accordance with Grube's view that the overvoltage at a platinum anode is due to the formation of an oxide of platinum.

Experiments have also been made with a cell constructed according to Pouzenc's patent, with a continuous flow of electrolyte between vertical electrodes, but perborate has not been obtained.

C. H. D.

Oxidation and Deterioration of Coal. ALVIN J. COX (*Philippine J. Sci.*, 1912, **7**, [A], 297—314).—An account is given of experiments which have been made with various types of Philippine coal in order to ascertain the deterioration which occurs as a result of storage. In particular, information was sought with respect to the extent to which oxygen is absorbed and the rate at which this takes place. For this purpose the carefully prepared samples were exposed to air or oxygen in a closed apparatus, to which was attached an adjustable barometer tube by means of which changes of pressure in the containing vessel could be followed at will. The composition of the gas in contact with the coal before and after storage was also determined.

The results obtained show that the exposure of coal to air or oxygen is at first accompanied by a diminution of the gas pressure, but that subsequently the pressure increases with the time of exposure. The reduction is due to the absorption of oxygen, and the subsequent increase to the evolution of carbon dioxide. The observations show clearly that the production of carbon dioxide is not simultaneous with the absorption of oxygen, and it is suggested that intermediate peroxides are formed. The rate of absorption of oxygen by a given coal varies according to its previous exposure to the air. Under the same conditions it depends on the size of the grains, and increases with the extent of the surface exposed.

Measurements were also made of the calorific values of the original and stored samples of the coals. When the data are reduced to an ash- and water-free basis, it is found that in all cases the calorific value is reduced by prolonged storage in contact with air. Some observations made on coal samples stored in nitrogen and in carbon dioxide indicate that there is no deterioration in these circumstances.

H. M. D.

Velocity of Flame in Mixtures of Inflammable Gases and Air. M. Hofsäss (*Chem. Zentr.*, 1915, i, 872; from *J. Gasbeleucht.*, **58**, 73—75).—The gases under investigation were prepared by the carburation of air with the vapours of pentane, hexane, benzene, gasolene, and light petroleum. The gas flowed through a burner consisting of a brass tube of circular section, and the height of the inner cone of the Bunsen flame produced is a measure of the velocity of propagation, the rate of flow of the gas in the tube being known. The maximum velocity of propagation is greater the lower the electric dissociation constant. The velocity increases with the proportion of air to a maximum, and then rapidly decreases, so that a very slight increase in the quantity of air at this stage causes the flame to go out. G. F. M.

Influence of Secondary Air on the Inner Cone of the Bunsen Flame. L. Ubbelohde and O. Dommer (*Chem. Zentr.*, 1914, ii, 1379). —Secondary combustion exercises a marked influence on the primary combustion in the inner cone. The authors have determined the total influence by estimating the velocity of ignition and the flame temperature, both with divided and undivided flames. In a burner 0·7 cm. wide the velocity of ignition is affected from about 60% CO downwards, the flame temperature from about 45% CO. With 70% CO the former is about 30% greater, the latter about 20% higher, in the undivided than in the divided flame. The composition of the intermediate gases has been investigated at several points in the CO flame. With the burner mentioned above, secondary combustion products are formed in the inner cone when the gas supplied contains 50% or less of carbon monoxide, and their amount increases with great rapidity with diminution in the supply of primary air. The form of the flame, the course of the introduction of secondary air, and the distance of the zones of combustion have a marked effect on the composition of the intermediate gas, the temperature, and the velocity of ignition. The maximum temperature of the CO flame is not obtained with the stoicheiometric mixture. Access of unexpectedly large volumes of secondary combustion products and of secondary air to the intermediate gases is of practical importance, since dilution of the latter lowers the temperature of the flame in consequence of the increased flame-volume. For the attainment of high temperatures, the theoretical mixture is most profitable, since, on the one hand, in consequence of the high primary air content, the volume of the flame is but little increased by secondary products, whilst, on the other hand, the tensely burning flame tends largely to resist the access of secondary products. H. W.

Combustion in the Inner Cone of the Bunsen Flame. L. Ubbelohde and O. Dommer (*Chem. Zentr.*, 1914, ii, 1379—1380. Compare preceding abstract).—The authors are led to the following conclusions: The dissociation equilibrium of carbon dioxide and water-vapour is not attained immediately above the inner cone in the case of air-gas flames, and is least complete with mixtures of

carbon monoxide and air. The difference between the thermodynamic and thermoelectrically measured temperatures is about 500° in this flame when the stoicheiometric mixture is employed, about 200° with the methane flame, about 130° with acetylene, and about 70° with hydrogen or coal gas. Only about 80% of the primary mixture of carbon monoxide and oxygen reacts immediately at the inner cone of the CO-flame, whilst 20% passes this region unburnt and reacts outside it. The combustion of the carbon monoxide appears to be a trimolecular reaction. The velocity of the reaction is much greater on the surface of the inner cone than outside it. When oxygen is added to the mixture of air and gas, the equilibrium is more readily attained, and this can also be effected by previously warming the unburnt gas. Platinum or an Auer mantle catalyses the combustion, and causes attainment of equilibrium. In all flames in which carbon monoxide is burnt, the thermoelectrically measured temperature of the inner cone does not agree with that calculated from the calorific value and specific heat; for example, in the CO-air flame about 15% of the energy of the gases appears to be lost. In the hydrogen flame, on the other hand, the agreement between the calculated and observed values is fairly good, the difference being only about 4%. For this reason also, the hydrogen flame is considerably hotter than that of carbon monoxide, although according to theory the reverse is to be expected. Similarly, mixtures of coal gas and hydrogen yield hotter flames than those of coal gas and carbon monoxide. Experiments on the influence of moisture on the combustion of carbon monoxide show that the velocity of ignition is more than trebled by admixture of 7—10% of water-vapour; the temperature of ignition is lowest with about 1%. The addition of oxygen enormously increases the velocity of ignition. Previous warming has a similar effect, and also widens the limits of explosibility.

It is further shown that the methane content of the smoke gases (the gas leaving the inner cone) does not correspond with the equilibrium mixture for the flame temperature. When methane is present in the fresh gas it would therefore appear to be incompletely burnt in the inner cone; in the case of acetylene and ether flames, it must be assumed that methane is formed at the beginning of the combustion, and that it then escapes from the inner cone before sufficient time has elapsed to ensure its decomposition. The phenomena of aureoles is not caused by the temperature, since an effect similar to that observed in the CO-flame could be observed about 500° below the ignition temperature. It is very probable that it is due to after-combustion in the intermediate gas. H. W.

Tellurides of Silver and Gold. Giovanni Pellini (*Gazzetta*, 1915, **45**, i, 469—484. Compare Pellini and Quercigh, A., 1910, ii, 1063; 1911, ii, 45).—The author has made a thermal investigation of the ternary system Ag–Au–Te, more especially of the partial system, Ag_2Te–$AuTe_2$–Te, which is of interest in view of the numerous natural double tellurides of silver and gold. The mixtures were protected from oxidation by means of a current of nitrogen.

The system Ag_2Te–$AuTe_2$ was first studied, the durations of the eutectic arrests during cooling indicating the formation of a new compound, $(Ag,Au)_3Te_2$, analogous to one of the sodium tellurides (A., 1910, ii, 1062); the existence of a mineral of this type has not yet been observed.

The triangular diagram for the system Ag_2Te–$AuTe_2$–Te indicates that the compounds AgTe and $(Ag,Au)_3Te_2$ melt with decomposition as well into the binary system as into the ternary system, since on the transversal AgTe–$AuTe_2$ the compound AgTe does not crystallise first, and on the transversal $(Ag,Au)_3Te_2$–Te the compound $(Ag,Au)_3Te_2$ does not crystallise first; the surface of primary crystallisation of Ag_2Te passes beyond these transversals. The ternary system considered presents four points of invariant equilibrium: (*a*) at about 412° and the atomic proportions, 52Te + 44·7Ag + 3·3Au, represented by three solid phases, α- and β-AgTe and Ag_2Te, and the liquid fusion; (*b*) at about 385° and the atomic concentrations, 53Te + 42·7Ag + 4·3Au, represented by three solid and one liquid phases, the compound Ag_2Te reacting with the fused mass of concentration *b* to form the compounds α-AgTe and $(Ag,Au)_3Te_2$; (*c*) at about 340° and the atomic proportions 57Te + 37Ag + 6Au, represented by three solid and one liquid phases, the compound $(Ag,Au)_3Te_2$ reacting with the fused mass of concentration *c* to form α-AgTe and $AuTe_2$; (*d*) at 335° and the atomic concentrations, 60Te + 35Ag + 5Au, this being a ternary eutectic point represented by three solid phases, α-AgTe, $AuTe_2$, and Te, and the fused mass. At lower temperatures all the alloys are completely solid. The crystallisation phenomena of the ternary system give rise to nine curves of univariant equilibrium, these dividing the concentration triangle into six zones. T. H. P.

Method of Reducing Some Metals in Crystalline Form on Glass Slips as Permanent Microscope Mounts. Jas. H. Bowman (*J. Amer. Chem. Soc*, 1915, **37**, 1468—1471).—If a thin film of a mixture of equal parts of 10% silver nitrate solution and concentrated zinc nitrate solution is spread on a glass slip and zinc filings are allowed to fall evenly on the moist surface, each zinc particle becomes a centre for the formation of radiating, fern-like crystals of silver. The slip is placed on a piece of damp filter-paper, and covered with a bell-jar in order to retard evaporation until crystallisation is complete. The slip is afterwards removed and left in the air until it is nearly dry. A few drops of solution of Canada balsam in xylene are then run over the slip, and when dry the preparation can be mounted with Canada balsam in the usual way.

In a similar manner, crystals of gold, copper, lead, bismuth, tin, and cadmium may be prepared. They form brilliant, microscopic objects when viewed by reflected light. E. G.

The Hardness of Solid Solutions. Cecil H. Desch (*Trans. Faraday Soc.*, 1915, **10**, 251—255).—The principal pairs of metals which form continuous series of solid solutions with one another are

of small atomic volume, the atomic volumes of the two components being nearly equal in each case. The hardness is always a maximum near the middle of each series. In the magnesium–cadmium series, in which the compound MgCd occurs in the middle of a continuous series of solid solutions, there are two maxima in the hardness curve, corresponding with the largest proportions of foreign molecules. The possible explanations of these facts are discussed. C. H. D.

Solubility of Magnesium Carbonate in Natural Waters. ROGER C. WELLS (*J. Amer. Chem. Soc.*, 1915, **37**, 1704—1707).—A study of the solubility of magnesium carbonate under ordinary atmospheric conditions has shown that the same result can be obtained by starting either with a solution containing an excess of magnesium hydrogen carbonate or with the pure trihydrate and water. The solution finally contains 0·36 gram of magnesium and 1·01 grams of carbon dioxide per litre at 20°. The solubility of natural magnesite, however, is only 0·02 gram of magnesium and 0·07 gram of carbon dioxide per litre. Certain natural waters, freely exposed to the atmosphere, seem to be supersaturated with respect to magnesite, but none of them approaches very closely to the point of saturation of the trihydrate. E. G.

Period of Induction and Passivity of Zinc. M. CENTNERSZWER and JUL. DRUKKER (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 439—469).—The following further results have been obtained (compare Centnerszwer and Sachs, A., 1914, ii, 550). Active zinc is covered with a layer of the spongy metal, which is formed only in reactions in which hydrogen is liberated. Removal of this layer results in a new induction period, the passivity being then greater than that caused by polishing with fine emery. By treatment with 10*N*-sodium hydroxide, zinc is rendered completely active, whereas a distinct induction period is always observed with zinc activated by iodine solution. Experiments made with zinc from which the adherent surface layer of air has been removed indicate that induction is not conditioned by imperfect wetting of the surface. Zinc is rendered passive to a high degree by heating in a vacuum or in a current of hydrogen, and this passivity is not merely superficial, but extends into the depths of the metal, since treatment with emery removes it only partly, and not to the same extent as with zinc not previously heated. The presence of ferrous sulphate shortens the induction period, and greatly increases the maximum velocity of solution.

Measurements have been made of the velocities of dissolution of zinc in very dilute hydrochloric and sulphuric acids of various concentrations by means of Ostwald's chemograph (A., 1900, ii, 730; 1901, ii, 24). The results show that the prolongation of the induction period, and also the maximum velocity of dissolution finally attained, depend on the nature and concentration of the acid employed. The induction period is lengthened by dilution of the acid, but as the velocity of dissolution, in dilute acids especi-

ally, increases only very slowly, this period is incapable of exact determination, the radius of curvature of the velocity curve being very great in the neighbourhood of the maximum. Amalgamated zinc exhibits extraordinarily high passivity, and is not dissolved appreciably by N-hydrochloric acid. This result is noteworthy on account of the fact that amalgamated aluminium dissolves appreciably more readily than the untreated metal, and even decomposes pure water.

The potential of polished zinc plates increases on dissolution, but the increase soon reaches a limiting value of about 0·02 volt. In every case passive zinc is found to be more noble than the active metal. Passive zinc is activated by cathodic polarisation, and active zinc is rendered passive by anodic polarisation, in spite of the accompanying dissolution of the surface layer.

These results confirm the analogy between the passivity of zinc and that of iron. T. H. P.

Displacement by Zinc of Metals from Solutions of their Salts. M. Centnerszwer and Jul. Drukker (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 528—536).—A zinc plate, attached by means of wax to a glass stirrer, was kept in continual motion in a solution of copper sulphate of definite initial concentration, the alteration in the latter being determined at regular intervals by titration with $N/100$-sodium thiosulphate solution. Experiments were made with $N/100$- and $N/20$-copper sulphate solution at the ordinary temperature and at 25°, the surface of the zinc being polished in all cases.

According to the theory of diffusion, the course of a reaction in a non-homogeneous medium is determined solely by the velocity of diffusion in the limiting layer, provided that the chemical process between the two phases proceeds sufficiently rapidly. In the case considered, the speed of diffusion may be assumed to be proportional to the difference in concentration of the copper sulphate in the solution and at the surface of the metal. If the former is indicated by c and the latter by c_0, and the velocity of reaction is measured by the amount of copper precipitated, x, the following equation holds, $dx/dt = k \,.\, F(c - c_0)$, F representing the surface of the zinc plate. If the reaction at the surface of the zinc is instantaneous, $c_0 = 0$, and, consequently, $dx/dt = k \,.\, F \,.\, c$. Further, if C is the initial concentration of the solution and v its volume, $x = (C - c)v$, and $dx/dt = -v \,.\, dc/dt$. From this follows the equation, $-v \,.\, dc/dt = k \,.\, F \,.\, c$, and this, on integration, gives

$$k = 2{\cdot}303v(\log C - \log c)/F \,.\, t.$$

The results obtained show that the velocity constant of the reaction increases during the first half hour, but that there is no sharply defined period of induction. The reaction follows the equation of the first degree, as is required by the theory of diffusion, so that its velocity is proportional to the first power of the concentration of the copper sulphate.

Further experiments have been made to determine the lapse of time between the immersion of the zinc and the commencement of

the deposition at its surface of the other metal, solutions of copper sulphate and of nickel and cobalt chlorides, sulphates, and nitrates being employed. The zinc cylinders used were coated with wax, excepting over one end surface, which was polished and arranged uppermost in the liquid in order to admit of examination under a lens. It is found that zinc reacts with copper salts far more rapidly than with those of nickel and cobalt, and that in solutions of chlorides the action begins decidedly earlier than in solutions of the corresponding sulphates. With nickel and cobalt nitrates no action occurs (compare Sackur, A., 1904, ii, 721; 1909, ii, 305), although in a concentrated solution of the former a precipitate of the hydroxide gradually appears. In solutions of copper sulphate the reaction does not give rise to liberation of gas, but in nickel chloride and sulphate solutions deposition of the metal is followed some time later, and in cobalt chloride, very considerably later, by evolution of gas bubbles. This gas is probably hydrogen, resulting from the decomposition of water by the zinc–nickel or zinc–cobalt couple. The deposition of the metal is not influenced by the presence of NO_3' ions, and two equivalent solutions containing (1) nickel sulphate and potassium nitrate, and (2) nickel nitrate and potassium sulphate gave identical results.

The conclusion is drawn that a period of induction is observed, not only in the replacement of hydrogen, but also in that of metals by zinc. In the latter case, however, this period is far shorter than in the former, and is noticeable only with very dilute solutions of the salts. It follows, therefore, that the retardation of the dissolution of zinc in acids during its initial period is due to the difficulty with which the hydrogen ions are converted into gaseous hydrogen, and to the resistance offered by the dielectric layer formed by the discharge of the hydrogen ions at the surface of the electrode (compare Centnerszwer and Sachs, A., 1914, ii, 550).

In the displacement of metals by zinc, "local elements" are formed very shortly after the initial deposition of the metal on the zinc (compare Ericson-Aurén and Palmaer, A., 1902, ii, 64; 1903, ii, 718), the velocity of the reaction being proportional to the sum of the currents of all these cells. Since the resistances of the latter are small, the electrochemical interchange of metals proceeds with great rapidity, and the velocity of the reaction is conditioned solely by the rate of diffusion of the dissolved salt from the solution to the surface of the zinc; in this phase, therefore, the reaction follows the theory of diffusion.

In the displacement of hydrogen by metals, the bubbles of hydrogen pass away from the surface of the metal, and the cause of the establishment of local cells is, therefore, absent. Such local galvanic elements may, however, be formed in this case (1) in consequence of the presence of admixed metals (compare De la Rive, *Ann. Chim. Phys.*, 1830, **43**, 425), and (2) owing to solution of hydrogen in the zinc (compare preceding abstract). Since both of these causes act very slowly, the period of induction is greatly prolonged in this case. T. H. P.

The Hardening of Metals. G. T. Beilby (*Trans. Faraday Soc.*, 1915, **10**, 212—215).—Pure ductile metals may be hardened by cold-working, or by admixture with other metals or non-metals. These mixtures or alloys may, if ductile, be further hardened by cold-working, whilst certain of them may be hardened by chilling. Chilling, again, may act by stereotyping the structure which is stable at a high temperature, or by setting up contraction strains within the metal or alloy.

The study of the mechanical hardening of pure gold, silver, or copper has the advantage of dealing with very simple, probably monatomic, molecules. In the hard, vitreous condition the atoms or molecules are arranged heterogeneously as regards their polarities, and as the temperature rises orientation occurs. The vitreous character of the "flowed" metal is best accounted for by assuming actual liquefaction and rapid resolidification during cold-working, resulting in the production of internal elastic strains. C. H. D.

Alloys of Manganese and Bismuth. N. Parravano and U. Perret (*Gazzetta*, 1915, **45**, i, 390—394).—Wedekind and Weit (A., 1911, ii, 985) and Hilpert and Dieckmann (A., 1911, ii, 1090) have prepared the crystalline compound, MnBi, and Bekier (*Int. Zeitsch. für Metallographie*, 1914, **7**, 83) has investigated the diagram of state of Mn–Bi alloys. The results of the authors' examination of this diagram are essentially identical with those obtained by Bekier, and show that the two metals are partly miscible in the liquid condition, and form a compound which originates by peritectic reaction at about 450°. With reference to the concentrations of the two liquid strata in equilibrium at a high temperature and also as regards the composition of the compound, the authors' data differ from Bekier's figures. The invariant temperature is found to be 1238°, and the proportions of manganese in the two equilibrated mixtures 30% and 93% respectively. Study of the cooling curves for mixtures of various compositions shows that the maximal thermal effect occurs with an alloy containing 20% of manganese, which corresponds well with the compound MnBi. Crystals were also separated which gave, on analysis, 20·42% of manganese and 80·1% of bismuth. T. H. P.

The Influence of Allotropy on the Metastability of Metals, and its Bearing on Chemistry, Physics, and Technics Ernst Cohen (*Trans. Faraday Soc.*, 1915, **10**, 216—239).—A summary of work previously published (A., 1914, ii, 52, 135, 202, 652, 799). C. H. D.

The Hardening of Metals by Quenching. C. A. Edwards (*Trans. Faraday Soc.*, 1915, **10**, 248—250. Compare A., 1913, ii, 120). —The hardness of quenched metals is attributed to the internal stresses set up in quenching, resulting in the formation of a very large number of twin lamellæ, amorphous layers being produced. The objections to this view are discussed. C. H. D.

The Part Played by the Amorphous Phase in the Hardening of Steels. J. C. W. Humfrey (*Trans. Faraday Soc.*, 1915, **10**, 240—247).—The hardness of quenched steels is attributed to an amorphous solution of iron carbide in α-iron. It is assumed that the passage of one crystalline allotropic modification into another takes place through an intermediate amorphous state, corresponding with the liquid phase of the modification about to be formed. The $\gamma \longrightarrow \alpha$ change in iron may be delayed by sudden cooling or by the presence of certain alloyed elements until the temperature is so low as to hinder recrystallisation when the amorphous phase is retained in a metastable state. C. H. D.

Crystal Twinning and the Martensitic Structure. Cecil H. Desch (*Trans. Faraday Soc.*, 1915, **10**, 255—256).—By slow cooling of an overheated steel a form of martensitic structure may be obtained, without any increase of hardness. The structure consists of pearlite, arranged parallel to certain planes of the original γ-crystal. The martensitic structure of a quenched steel is probably an accompaniment, and not the cause, of its hardness. C. H. D.

The Interstrain Theory of Hardness. Andrew McCance (*Trans. Faraday Soc.*, 1915, **10**, 257—264).—An examination of the hardening of different varieties of steel from the point of view that hardness is due to interstrain, this term being adopted to avoid any assumption as to the nature of the hardened material. C. H. D.

Hardening with and without Martensitisation. Henry M. Howe (*Trans. Faraday Soc.*, 1915, **10**, 265—270).—A martensitic structure is produced by rapidly cooling carbon steel, by moderate cooling of steel with an intermediate proportion of manganese and nickel, by re-heating austenitic manganese steel, and by cooling 25% nickel steel in liquid air. Manganiferous austenite is hardened without the formation of austenite by heating at 550°, which is below the transformation temperature, and the hardness is independent of the rate of cooling. This fact is not readily explained by any form of the amorphous metal hypothesis, and is most consistent with the theory of hard β-iron. Steel containing 0·02% of carbon does not show any martensitic structure when etched with hydrogen chloride within the β-range of temperature. C. H. D.

The Hardening of Steel. J. O. Arnold (*Trans. Faraday Soc.*, 1915, **10**, 272—274).—The hardness of steel is attributed solely to the presence of the solid solution of iron and iron carbide, hardenite, which has the hardness of quartz. The influence of other metals on the transformation temperature is discussed. C. H. D.

The Hardening of Metals. Sir Robert Hadfield (*Trans. Faraday Soc.*, 1915, **10**, 207—211).—An introduction to a general

discussion. A piece of ancient Indian steel, in the form of wedges found between the foundation slab and the base of the stone column of Heliodorus, at Besnagar, dating from 125 B.C., is described. The average composition of the steel is: carbon, 0·70%; silicon, 0·04%; sulphur, 0·008%; phosphorus, 0·020%; manganese, 0·02%; chromium and nickel, traces, but the carbon is seen on microscopical examination to vary locally from 0·30 to 0·75%. The structure is pearlitic, and somewhat irregular. It is rendered martensitic and glass-hard by quenching from 850°. As the inscription shows that the pillar was erected by a Greek ambassador, it is possible that the steel was forged by Greeks. C. H. D.

The Chemical and Mechanical Relations of Iron, Cobalt, and Carbon. J. O. ARNOLD and A. A. READ (*Proc. Inst. Mech. Eng.*, 1915, 247—293. Compare Ruff and Keilig, this vol., ii, 465).—Steels containing cobalt, prepared by melting together Swedish bar iron, Swedish white iron, and aluminothermic cobalt, are dissolved electrolytically in dilute hydrochloric acid, D 1·02, using a low current density. Practically the whole of the carbon of the steel remains in the carbide residue. Cobalt carbide, Co_3C, forms a series of solid solutions with iron carbide, Fe_3C. These solutions are very stable on annealing. A steel containing 0·64% of carbon and 2·68% of cobalt only contains a trace of graphite after annealing for eight hours at 780°. Nickel carbide in steels is less stable. In the absence of iron, cobalt carbide is very unstable. C. H. D.

Negative Colloidal Ferric Hydroxide. FRANK POWIS (T., 1915, **107**, 818—824).—Ferric hydroxide has been usually regarded as a typical positive colloid. As usually prepared, the colloidal particles certainly carry an excess of positive charge, but the author shows that this may be converted into a negative charge by suitable modification of the method of preparation. If the particles are formed in a solution which tends to give a negative potential difference, a negative colloid is obtained. This may be effected by adding slowly 100 c.c. of 0·01*N*-ferric chloride to 150 c.c. of 0·01*N*-sodium hydroxide, the solution being continuously shaken during the process. On the other hand, if the sodium hydroxide is added to an excess of the ferric chloride solution, a positive colloid is obtained. The negative colloid may be converted into the positive if a solution of the former is added to a very dilute solution of sodium hydroxide (0·005*N*) with constant shaking.

In regard to the potential difference at the surface of colloidal particles, it is supposed that this is due to the adsorption of ions from the solution, and that its sign depends on whether the cations or anions are in excess in the layers in close proximity to the particles. In the case of dialysed colloids the potential difference is due to traces of residual electrolyte, and if these were removed the potential difference would be zero. H. M. D.

Action of Dilute Solutions of Acids, Alkalis, and Salts on Certain Metals. A. J. HALE and H. S. FOSTER (*J. Soc. Chem. Ind.*, 1915, **34**, 464).—The authors have compared the amounts of corro-

sion suffered by sheets of zinc, cast iron, wrought iron, aluminium, lead, copper, tin, and nickel, when immersed in 0·2*N*-solutions of nitric, hydrochloric, and sulphuric acids, sodium and ammonium hydroxides, sodium carbonate, and sodium, calcium and magnesium chlorides.

The results agree in the main with published statements, but the following facts are emphasised: (1) Copper is attacked much more by dilute hydrochloric acid than by nitric or sulphuric acids, which have about the same corrosive action. (2) Aluminium is slowly attacked by dilute nitric and sulphuric acids. (3) Lead is more rapidly attacked by hydrochloric acid than by sulphuric acid, the effect of which is negligible. (4) Tin is soluble in sodium hydroxide or carbonate, but not in ammonia. J. C. W.

Potassium Antimonides. N. Parravano (*Gazzetta*, 1915, **45**, i, 485—489).—The author has investigated the melting-point diagram of potassium–antimony alloys, the experiments being carried out in an atmosphere of dry hydrogen. Fusion of the potassium under a mixture of light petroleum and vaselin oil, with the object of removing the film of oxide, results in separation of the metal in globules, from which it is difficult to obtain a compact mass. Satisfactory results are, however, obtained by removing the oxide mechanically under benzene, immersing the metal for a short time in benzene containing a little amyl alcohol, and washing it with ether.

The melting-point diagram is very simple, and shows that two compounds, K_3Sb and KSb, with sharp melting points, are formed. The formation of these compounds is accompanied by the development of a considerable amount of heat, and, in the former case, is of almost explosive violence. Eutectic arrests at 485°, 400°, and 63° are observed in all the mixtures, the formation of solid solutions of the compounds with their components being excluded. The eutectic, $K_3Sb + KSb$, at 485° solidifies with supercooling in presence of K_3Sb, but not in presence of KSb. The *compound*, K_3Sb, m. p. 812°, is yellowish-green and iridescent, and undergoes rapid change in the air; when broken it usually ignites spontaneously. The *compound*, KSb, m. p. 605°, forms long, slender prisms of the colour of antimony, oxidises in the air less readily than the preceding compound, and does not ignite spontaneously even when struck with a hammer.

Mathewson (A., 1906, ii, 666) found that, with elements of the second group, sodium forms compounds increasing in number with the atomic weight of the second metal; this rule does not, however, hold good for the elements of the fourth and fifth groups. On the other hand, the rule is followed by the compounds of potassium with elements of the fifth group, one compound being formed with nitrogen or arsenic, two with phosphorus or antimony, and four with bismuth. With reference to the compound described by Smith (A., 1907, ii, 949) as K_9Bi_7, it is pointed out that, since this compound results from a peritectic reaction and the duration of the reaction cannot furnish an absolute criterion of the composi-

tion, and since, further, the latter was not confirmed by analysis, it is not improbable that the true formula is KBi. T. H. P.

New Series of Quadrivalent Platinum Compounds (Chloropentammineplatinum Compounds). L. TSCHUGAEV and N. VLADIMIROV (*Compt. rend.*, 1915, **160**, 840—842).—The authors have prepared a series of salts corresponding with the base

$$[PtCl(NH_3)_5](OH)_3.$$

By the action of liquid ammonia on ammonium platinichloride, in the absence of water, in sealed tubes at the ordinary temperature there is obtained a mixture of the chloride, $[Pt(NH_3)_6]Cl_4$, and *chloropentammineplatinic chloride*, $[PtCl(NH_3)_5]Cl_3$, of which the former is the less soluble. By the action of concentrated nitric acid on this new chloride, *chloropentammineplatinic nitrate*, $[PtCl(NH_3)_5](NO_3)_3$, is obtained; it is less soluble than the chloride. The corresponding *carbonate* and *sulphate* have been prepared, and these are almost entirely insoluble in water, but are easily soluble in the fixed alkalis. The tervalency of the ion $[PtCl(NH_3)_5]'''$ has been confirmed by measurements of the conductivity of the salts in solution, and also by their power to coagulate colloidal solutions of arsenic trisulphide. All of these salts on reduction with zinc and dilute hydrochloric acid yield the corresponding salts of Reiset's base, $[Pt(NH_3)_4]X_2$. W. G.

Mineralogical Chemistry.

Identity of Footeite with Connellite: Two New Occurrences of the Mineral. W. E. Ford and W. M. Bradley (*Amer. J. Sci.*, 1915, [iv], **39**, 670—676).—A re-examination of the original material, described by G. A. Koenig in 1891 as footeite, from Copper Queen mine, Bisbee, Arizona, proves its identity with the Cornish connellite. The mineral is also described from the Czar mine at Bisbee (anal. I), and from the Grand Central mine at Eureka, in the Tintic district of Utah (anal. II). At both these localities it occurs under very similar conditions, forming tufts of bright blue needles in cavities in massive cuprite, and associated with chrysocolla, malachite, spangolite, etc. The crystals are hexagonal with refractive indices, $\omega = 1{\cdot}730$ and $\epsilon = 1{\cdot}754$.

	CuO.	Cl.	SO_3.	N_2O_5.	H_2O.	Total (less O for Cl).
I.	73·38	6·82	3·15	0·72	17·13	99·67
II.	73·41	7·05	3·84	0·30	16·81	99·82

Formula, $16Cu(OH)_2,2CuCl_2,CuSO_4,3H_2O$. The small amount of nitrogen pentoxide perhaps replaces sulphur trioxide. Other copper minerals were examined for the presence of nitrogen pentoxide, but a trace only was found in atacamite, from Jerome, Arizona.

L. J. S.

Kainite from Kalusz. WINCENTY KOLSKI (*Chem. Zentr.*, 1915, i, 271; from *Zeitsch. landw. Vers.-Wesen Österr.*, 1914, **17**, 892—901).—Analyses of specimens of kainite from the Kalusz Works in Eastern Galicia gave the following mean results: K_2O, 9—11%; Cl, 29%; SO_3, 17·5%. The sodium content showed great variation (8—20%). In one specimen, 0·65% Mn_3O_4 was found. H. W.

Relations Existing between the Chemical, Optical, and Other Physical Properties of the Members of the Garnet Group. W. E. FORD (*Amer. J. Sci.*, 1915 [iv], **40**, 33—49).—The index of refraction, density, molecular weight, and composition of the following members of the garnet group are considered: pyrope, grossularite, hessonite, almandite, spessarite, uvarovite, and andradite. It is shown that both the index of refraction and the density depend in a simple and direct manner on the composition. The relationships between density, refractive index, and molecular weight are fairly constant until the andradite molecule becomes predominant. This causes a distinct break in the continuity of these relations. There is a definite relationship between refractive index and density in many cases, but a large number of inexplicable exceptions are observed. J. F. S.

Nephelite Crystals from Monte Ferru, Sardinia. H. S. WASHINGTON and H. E. MERWIN (*J. Washington Acad. Sci.*, 1915, **5**, 389—391).—An account is given of the crystallographic and optical examination of small, well-formed crystals of nephelite from Monte Ferru. Analysis of the crystals gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	Na_2O.	K_2O.	Insoluble.	Total.
40·27	31·05	2·42	0·81	15·11	3·22	7·51	100·39

H. M. D.

Observations on the Chemical Composition of Certain Minerals. FERRUCCIO ZAMBONINI (*Chem. Zentr.*, 1915, i, 1082).—The minerals of the *nepheline* group exclusive of the chloride–sulphates, and carbonate–silicates which form the sub-group *cancrinite*, contain the following chemical individuals: $K_2Al_2Si_2O_8$, $Na_2Al_2Si_2O_8$, $CaAl_2Si_2O_8$, Na_2SiO_3, $NaAlO_2$. Among the constituents of the *augites* are the compounds $R^{II}SiO_3$, $R^{II}R_2^{III}O_4$, $R^{II}R_2^{III}(SiO_3)_4$, where R^{II} is Ca, Mg, Fe'', Mn, or Na_2, and R^{III} is Al, Fe''', Cr'''. The rhombic *pyroxenes* consist of metasilicates of di- and ter-valent elements and an aluminate. The triclinic pyroxene, *babingtonite*, is polymorphous with the above; the calcium is here a more important constituent than in the rhombic pyroxenes. G. F. M.

Analytical Chemistry.

Notes on Quantitative Microanalysis. JULIUS DONAU (*Monatsh.*, 1915, **36**, 381—390. Compare A., 1913, ii, 424).—A further description is given of apparatus which has been devised for the carrying out of the processes of gravimetric analysis with very small quantities of substance. This includes apparatus for precipitation, filtration, evaporation, drying, heating, and weighing. H. M. D.

Simple Burette Reader. L. S. PRATT (*J. Amer. Chem. Soc.*, 1915, **37**, 1730—1731).—A simple device is described which facilitates the reading of burettes. It consists of a disc of mirror glass, about 35 mm. in diameter with the silvering removed from a rectangular section, about 4×10 mm. A thin, diamond-line extends across the face of the disc at right angles to the longer axis of the rectangle. The disc is held flat against the back of the burette, and so adjusted that the diamond-line coincides with the graduation next below the meniscus. By moving the eye up and down and also moving the disc slightly, the reflexion of the graduation is made to coincide with the diamond-line. The line of sight is then normal to the burette, and parallax is avoided; the meniscus appears sharp, black, and constant. E. G.

New Analytical Suction Filter. JOKICHI TAKAMINE, Jun. (*J. Amer. Chem. Soc.*, 1915, **37**, 1519—1520).—An apparatus for filtration with suction is described. It consists of a cylindrical glass jar, $6\frac{1}{2}$ inches deep and $5\frac{1}{2}$ inches in diameter, with a suction side-tube near the top fitted with a stop-cock. The upper rim of the cylinder is ground, and has a pouring lip in the side opposite the suction-tube. On the inner surface of the cylinder about half-way down are three glass projections to support a perforated shelf. The cover of the cylinder has the rim ground to fit on to the rim of the jar, and has an opening in the middle, $1\frac{3}{4}$ inches in diameter, for the reception of the stopper which carries the funnel. For filtering small quantities of liquid, a beaker or crucible is placed on the shelf to receive the filtrate, but if large quantities are to be filtered the shelf may be removed and the liquid filtered directly into the jar itself.

This filter is not only very simple, but is most convenient in respect of speed, neatness, and accuracy. E. G.

New Method for the Estimation of Acidity and Alkalinity. I. TRAUBE (*Ber.*, 1915, **48**, 947—949. Compare this vol., ii, 87, 101).—An account of the author's method as applied to general purposes. Alkalis are estimated by the lowering of the surface tension of solutions of the salts of alkaloids with strong acids, and acids by the same action on the alkali salts of the higher fatty acids, sali-

cylic, benzoic, or other weak acids. The stalagmometer gives trustworthy results, especially for traces, in about five minutes, and the viscostagonometer in three minutes. J. C. W.

Rational Analysis [of Clay]. O. KALLAUNER and J. MATĚJKA (*Chem. Zentr.*, 1914, ii, 732; from *Sprechsaal*, 1914, **47**, 423).—Moisture (*T*) is estimated by drying the clay at 110—120°; the clay is then digested with cold hydrochloric acid (1 : 1), washed with water, and again dried. The loss in weight corresponds with the amount of acid-soluble substances (*I*). A portion of the dried clay is now used for the estimation of the loss on ignition (*G*), whilst another portion (2 grams) is heated at 700°, then digested with 150 c.c. of hydrochloric acid, and the insoluble portion (*R*) collected on a filter and washed with hot water. The filtrate is diluted to 500 c.c., and 100 c.c. of this solution are used for the estimation of the soluble silica, iron oxide, and alumina (m_1); the amount of clay-substance (*II*) is found by multiplying the sum of the iron oxide and alumina by 2·533. The insoluble residue (*R*) is treated with hydrofluoric acid and sulphuric acid; the mixture is heated until the sulphuric acid has been expelled, and the dissolved alumina (m_2) is estimated by precipitation with ammonia; its weight multiplied by 5·46 gives the quantity of felspar (*III*). If the clay contains an appreciable quantity of mica, potassium is estimated in the filtrates from the aluminium hydroxide precipitates, m_1 and m_2; let the amounts of K_2O be n_1 and n_2. The mineral constituents of the clay are then calculated as follows: Clay substance $(II) = 2{\cdot}533m_1 - 21{\cdot}505n_1$; felspar $(III) = 8{\cdot}882n_2 - 2{\cdot}728m_2$; quartz $= (T) - [(I) + (G) + (0{\cdot}861 \times II) + (0{\cdot}954 \times IV)]$; mica $(IV) = 8{\cdot}49n_1 - 4{\cdot}237n_2 + 3{\cdot}907m_2$. W. P. S.

Influence of Phosphoric Acid on the Estimation of Available Chlorine in Bleaching Powder. E. KEDESKY (*Chem. Zentr.*, 1915, i, 806—807; from *Mitt. Kaiserl. Materialprufgs.-Amt.*, 1914, **32**, 534—535).—Bleaching powder always contains a small quantity of ferric oxide, and this interferes with the iodometric estimation of the available chlorine. When the sample is treated with hydrochloric acid and potassium iodide, the ferric oxide is first converted into ferric chloride which reacts with the potassium iodide, liberating iodine, and thus causing the result for available chlorine to be too high. The addition of phosphoric acid or sodium phosphate prevents the action of the ferric salt on the potassium iodide. Hough has shown (A., 1910, ii, 457) that phosphoric acid prevents the action of ferric haloids on permanganate. W. P. S.

Detection of Hydrochloric Acid in Medical Practice. JOHANNE CHRISTIANSEN (*Zeitsch. Biol.*, 1915, **65**, 513—515. Compare this vol., ii, 364).—Polemical against Krummacher (*loc. cit.*). The author maintains that the formation of the red dye in Günzberg's test depends on a high concentration of hydrogen ions. H. W. B.

Detection of Hydrochloric Acid in Medical Practice. O. KRUMMACHER (*Zeitsch. Biol.*, 1915, **65**, 516).—Final reply of the author to Christiansen (preceding abstract), in which he states that on the chief points his view is in agreement with that of Christiansen.

H. W. B.

Estimation of Chlorides in Small Amounts of Body Fluids. FRANKLIN C. MCLEAN and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1915, **21**, 361—370).—The method is applicable to urine, blood, exudates, gastric juice, etc. Proteins when present are first removed best by heat-coagulation and the addition of "blood charcoal"; the filtrate is then precipitated with silver nitrate in the presence of nitric acid, the silver chloride filtered off, and the excess of silver titrated with standard potassium iodide in the presence of nitrous acid. The end-point is the first appearance of an olive colour, due to free iodine. Full directions are given, and the accuracy of the method is illustrated. It is not more accurate than Volhard's method for urine, but is valuable because only small quantities are needed.

W. D. H.

New Method of Estimating Bromine and Chlorine in Organic Compounds. P. W. ROBERTSON (T., 1915, **107**, 902—907).—The method consists in heating the substance with a mixture of chromic and concentrated sulphuric acids in a flask of about 70 c.c. capacity fitted with ground-glass connexions, and passing the evolved bromine and hydrogen bromide in the case of bromo-compounds, or chlorine, hydrogen chloride, and chromyl chloride in the case of chloro-compounds, into an alkaline solution of hydrogen peroxide, whereby alkali bromide and chloride are formed respectively, and can be estimated by titration by Volhard's method after acidification with nitric acid. In the case of chloro-compounds it is necessary to reduce the chromate in the absorption tube before titration. In exceptional cases of very volatile compounds, it may be necessary to interpose a short length of platinised asbestos between the decomposition flask and the absorption tubes.

G. F. M.

Detection of Iodine in Organic Iodo-derivatives and in Mixtures of them with Bromo- and Chloro-derivatives by means of Ammonium Bromide. III. ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1915, **50**, 803—808. Compare this vol., ii, 167, 365).—For the detection of iodine in many alkyl iodides, iodobenzene, *o*-, *m*-, and *p*-iodonitrobenzenes, etc., which do not yield iodine when heated alone, the general tests for halogens in organic compounds must be employed. The author finds, however, that ammonium bromide, or in some cases ammonium chloride, serves to demonstrate, in the dry way, the presence of iodine in organic iodo-derivatives, even when these contain nitro-groups or are mixed with large proportions of bromo- or chloro-derivatives or chloro- or bromo-nitro-compounds. Even the most stable iodo-derivatives, when heated in a long, narrow tube with ammonium bromide, give

violet iodine vapour, and, after cooling, a distinct reaction with starch. This test is carried out more rapidly and with far smaller amounts of substance than the ordinary tests. T. H. P.

Estimation of the (Hübl) Iodine Number. ALFREDO PAGNIELLO (*Chem. Zentr.*, 1915, i, 335; from *Giorn. Farm. Chim.*, 1914, **63**, 505—515).—The addition of ammonium carbonate to the thiosulphate solution used in the process considerably increases the stability of the solution, and does not interfere with the estimation; water previously boiled and free from carbon dioxide should be used in preparing the thiosulphate solution. W. P. S.

Permanganate and Iodometric Estimation of an Iodide in Presence of a Chloride and Bromide. O. L. BARNEBEY (*J. Amer. Chem. Soc.*, 1915, **37**, 1496—1507).—Various modifications have been suggested of the method of estimating an iodide by its oxidation to an iodate by means of potassium permanganate. The result can be obtained either by direct measurement of the amount of oxidising agent required or by the estimation of the iodate produced.

It is now shown that the direct titration of the iodide, in presence of a bromide and chloride, gives inaccurate results owing to the formation of bromine, chlorine, or hypochlorous acid. If manganous sulphate and phosphoric acid are present in the ferrous solution employed for removing the excess of permanganate, the liberation of bromine and chlorine is prevented, and the excess of ferrous iron added can be accurately estimated by titration with permanganate.

An iodide can also be estimated in presence of a bromide and chloride by adding potassium iodide to the solution after the final titration of the excess of ferrous sulphate with permanganate and titrating the liberated iodine with thiosulphate.

Both titrations can be made with a single sample. The iodometric method gives the most accurate results when only very small quantities of iodine are present. With moderate amounts of iodine both methods are convenient, rapid, and accurate. E. G.

Colorimetric Estimation of Sulphur in Pig-iron and Steel. G. MISSON SERAING (*Chem. Zentr.*, 1914, ii, 1122—1123; from *Österr. Zeitsch. Berg. Hüttenwesen*, 1914, **62**, 459—460).—One gram of the sample is placed in a conical flask, 10 c.c. of benzene (D 0·710) and 50 c.c. of hydrochloric acid (D 1·14) are added, and the mouth of the flask is covered with a disc of filter paper 5 mm. thick, which has been previously immersed in a solution containing 10 grams of arsenious acid and 30 c.c. of hydrochloric acid per litre, and then dried. An ebonite plate weighted with a lead block is placed over the paper disc. The hydrogen sulphide produces a yellow coloration on the disc, and comparison with the colorations given by known amounts of sulphur gives the quantity of the latter in the sample. W. P. S.

Oxidation of Substances containing Sulphur by Potassium Chlorate and Hydrochloric Acid. MAX FEDERER (*Zeitsch. physiol. Chem.*, 1915, **94**, 128—131).—The author finds Gauvin and

Skarzynski's method for the estimation of total sulphur in urine and other physiological fluids to be untrustworthy, for only about 8—12% of the neutral sulphur is oxidised by evaporation with potassium chlorate and hydrochloric acid. Of taurine, cystine, peptone, potassium taurocarbamate, and potassium thiocyanate only the latter undergoes oxidation to sulphuric acid to anything like the theoretical extent by this means. J. C. W.

Estimation of the Total Sulphur in Vegetable Products. D. J. DE JONG (*Chem. Weekblad*, 1915, **12**, 626—634).—A method adapted to the estimation of small amounts of sulphur in vegetable products. It consists in oxidising the substance with potassium permanganate in presence of alkali hydroxide, and precipitating the sulphur as barium sulphate. A. J. W.

Estimation of Nitrogen by the Kjeldahl-Folin-Farmer Method. VICTOR JOHN HARDING and FRANCIS H. S. WARNEFORD (*J. Biol. Chem.*, 1915, **21**, 69—71).—In view of the great value of the Folin-Farmer method for the estimation of nitrogen in biological work, the authors have attempted to apply this method to the needs of pure organic chemistry. Preliminary experiments on the estimation of nitrogen in carbamide indicate, however, that the average error amounts to about 0·5%, and further work in this direction was therefore abandoned. F. B.

The Folin-Farmer Method for the Estimation of Nitrogen. OTTO FOLIN (*J. Biol. Chem.*, 1915, **21**, 195—199).—The author replies to Bock and Benedict's criticism (this vol., ii, 105) of the Folin-Farmer colorimetric method for estimating nitrogen in urine, and maintains that the sources of error pointed out by these observers are either non-existent or may be easily avoided. The error, due to uncertainties in the colorimetric readings, may be reduced to considerably less than 1%. F. B.

Estimation of Nitric Nitrogen in Soils. E. R. ALLEN (*J. Ind. Eng. Chem.*, 1915, **7**, 521—529).—Reduction of the nitrates with Devarda's alloy in $N/10$-sodium hydroxide solution yields trustworthy results even when large quantities of organic substances are present; a small amount of the alloy is required, the reaction proceeds quietly, and the action of such dilute alkali solutions on organic matter is very slight. The apparatus described by Mitscherlich (A., 1909, ii, 614) should be used in the estimation. Reduction with Devarda's alloy in magnesia solutions, and the aluminium reduction method, do not give trustworthy results in the presence of much organic matter; separation of the nitric and organic forms of nitrogen is almost impossible when the reduction is carried out in strongly alkaline solution. W. P. S.

Modified Reduction Method for the Volumetric Estimation of Nitro-compounds A. J. BERRY and C. K. COLWELL (*Chem. News*, 1915, **112**, 1—2).—In the estimation of nitro-compounds by reduc-

tion with stannous chloride the following method of titrating the excess of the latter is described; it is based on the fact that the brownish-violet colour of copper sulphate solution containing an excess of hydrobromic acid is discharged when the copper is reduced. The nitro-compound is boiled with the addition of stannous chloride, hydrochloric acid, and potassium bromide for fifteen minutes in an atmosphere of carbon dioxide; the solution is then titrated with a strongly acid copper sulphate solution containing potassium bromide. At the end-point of the titration the liquid assumes an orange-yellow colour. The stannous chloride solution must be standardised against the copper sulphate solution at the time the estimation is made. W. P. S.

A Compact Kjeldahl Apparatus. HUGH GARNER BENNETT (*Chem. Zentr.*, 1914, ii, 559; from *Collegium*, 1914, 482—484).—The distillation apparatus described consists of a conical flask of about 1 litre capacity; it is provided with a still-head, which is connected directly by a bent glass tube with a vertical condenser 13 inches in height. The width of the whole apparatus does not exceed 18 inches. W. P. S.

Nessler Reagent. G. FRERICHS and E. MANNHEIM (*Chem. Zentr.*, 1915, i, 221; from *Apoth. Zeit.*, 1914, **29**, 972—974).—The following method of preparing Nessler reagent is described: 2·5 grams of potassium iodide and 3·5 grams of mercuric iodide are dissolved in 3 c.c. of water, 100 grams of 15% potassium hydroxide solution are added, and, after twenty-four hours, the clear solution is decanted. If the solution is not clear it may be treated with a small quantity of talc, and filtered through a sand-filter.
W. P. S.

Qualitative Reaction for the Detection of Nitrates. ALFRED TINGLE (*J. Soc. Chem. Ind.*, 1915, **34**, 393).—The formation of nitrosalicylic acids, which give intense colours with alkalis, when salicylic acid dissolved in sulphuric acid is heated with a nitrate, affords a quick, easy, widely applicable test for nitrates, of the same order of delicacy as the "brown ring" test.

The reagent contains 2 grams of salicylic acid in 30 c.c. of concentrated sulphuric acid. The solid to be tested is cautiously warmed with a slight excess of this solution, and a drop of the resulting liquid is rendered alkaline by concentrated potassium hydroxide on a white tile. If the substance under examination is a liquid, two or three drops are warmed with two or three drops of the reagent until acid fumes appear, and the cold residue is treated with alkali. The development of a yellow or orange colour indicates the presence of a nitrate. One drop of a 0·1% solution of potassium nitrate responds to the test. Haloids do not vitiate the results. J. C. W.

Suitability of the Lorenz-Neubauer Method for the Estimation of the Phosphoric Acid of Basic Slag Soluble in Citric Acid. H. DUBBERS and CELICHOWSKI (*Chem. Zentr.*, 1915, i, 218—219; from *Landw. Jahrbb.*, 1914, **47**, 71—78).—The authors

find that this method is untrustworthy, and cannot, therefore, agree with the statements of Lemmermann and Haussding as to its suitability for the estimation of phosphoric acid (A., 1914, ii, 676). Popp's iron–citrate method is to be preferred. W. P. S.

Estimation of the Phosphoric Acid of Basic Slag Soluble in Citric Acid by the Lorenz Method. F. Haussding with O. Lemmermann (*Chem. Zentr.*, 1914, ii, 506; from *Landw. Jahrb.*, 1914, **46**, 327—338. Compare A., 1914, ii, 676).—Further investigation of Lorenz's method afforded added proof that the method is trustworthy; it yields concordant results which are not influenced by the presence of citric acid, lime, iron, and silica in the solution. W. P. S.

Factor to be Used for the Calculation of the Phosphoric Acid in Neumann's Method. S. L. Jodidi (*J. Amer. Chem. Soc.*, 1915, **37**, 1708—1710).—A study of Neumann's method of estimating phosphorus has confirmed Heubner's view (A., 1914, ii, 675) that the calculated value, 0·554 mg., for the amount of phosphorus equivalent to 1 c.c. of 0·5*N*-sodium hydroxide is too low, and has shown that the factor 0·57 is very nearly accurate. E. G.

Precipitation of Phosphorus as Ammonium Phosphomolybdate in Presence of Sulphuric Acid. K. George Falk and Kanematsu Sugiura (*J. Amer. Chem. Soc.*, 1915, **37**, 1507—1515). —Neumann's method for estimating phosphorus in organic matter (A., 1903, ii, 243; 1905, ii, 68) is based on the oxidation of the material with a mixture of concentrated nitric and sulphuric acids, precipitation of the phosphorus as ammonium phosphomolybdate, and titration of the latter, after removal of ammonia, with standard sodium hydroxide solution. A study of this method has now been made with special reference to the influence of the sulphuric acid in the precipitation of the phosphomolybdate.

It has been found that the ammonium phosphomolybdate contains sulphate, an excess of molybdic acid, and no nitric acid, and that its composition may vary with the concentration of the reagents in the solution; the different factors recorded by different observers for the titration of the precipitate with alkali hydroxide are thus explained. The composition of the precipitate for a certain set of conditions was found to be:

$$4[(NH_4)_3PO_4,12MoO_3],(NH_4)_2SO_4,5MoO_3.$$

Satisfactory results can only be secured if the conditions of precipitation have been determined with known amounts of the phosphate and an empirical formula obtained. Otherwise, it is necessary that the phosphomolybdate precipitate should be dissolved and reprecipitated (compare Hibbard, A., 1914, ii, 145). E. G.

Incineration of Ammonium Magnesium Phosphate in Superphosphate Analysis. Guido Vecchi (*Chem. Zentr.*, 1915, i, 505; from *Arch. Farm. sperim.*, 1914, **18**, 333—334).—The author

recommends the addition of 3 c.c. of concentrated sulphuric acid to the superphosphate solution before the phosphoric acid is precipitated by the addition of "magnesia mixture." Ammonium sulphate is thus occluded in the precipitated ammonium magnesium phosphate, and its presence accelerates the ignition of the latter.

W. P. S.

Estimation of Phosphoric Acid in Vegetable Substances, Especially Crops, and in Phosphates. A. Stutzer and W. Haupt (*J. Landw.*, 1915, **63**, 46—49).—The vegetable substance, containing about 2 grams of dry matter, is heated in a Kjeldahl flask with 25 c.c. of sulphuric acid and two drops of mercury until colourless. The solution is then diluted with water, transferred to a conical flask, and treated with solid ammonium carbonate, by which the temperature is lowered instead of being raised, as with ammonium hydroxide. When the carbonate begins to dissolve slowly, an indicator is added, and then a strong solution of ammonium carbonate until the solution is neutral or slightly alkaline. It is then made acid with strong nitric acid, filtered if necessary, and heated until it begins to boil. Molybdic acid (100 c.c.) is added, and the solution filtered after two hours through asbestos in a perforated crucible, which is heated at 130—140° and weighed. The precipitate is washed with dilute nitric acid, followed by alcohol, dried at 130—140°, and gradually ignited until uniformly bluish-green, and weighed. The factor for calculating the amount of P_2O_5 is 0·03946. The molybdic solution is prepared by dissolving 250 grams of molybdic acid in 250 c.c. of 24% ammonia, and diluting to 2 litres; it is then slowly added to 4 litres of nitric acid, D 1·20.

Phosphates are precipitated in a similar manner after neutralising the solutions, containing hydrochloric or sulphuric acid, with ammonia, and acidfying with nitric acid. N. H. J. M.

Detection of Arsenic. O. Billeter (*Chem. Zentr.*, 1914, ii, 951—952; from *Mitt. Lebensmittelunters. u. Hyg.*, 1914, **5**, 280—287). —To detect arsenic in organic substances a suitable quantity of the material is treated in the usual way with a mixture of nitric and sulphuric acids, and the arsenic is separated from the residual sulphuric acid solution as follows: Four grams of sodium chloride, 1 gram of potassium bromide, and 0·2 gram of hydrazine sulphate are placed in a distillation flask connected with a condenser, and the sulphuric acid containing the arsenic is added from a tapped funnel. The mixture is then heated until gas ceases to be evolved, the distillate being collected in a receiver containing 50 c.c. of water and a few drops of hypochlorous acid. The distillate may be concentrated by evaporation without loss of arsenic, and is subsequently transferred to a Marsh apparatus. The method is capable of detecting 0·001 mg. of arsenic in 50 grams of substance.

W. P. S.

Rapid Organic Combustions. Marie Reimer (*J. Amer. Chem. Soc.*, 1915, **37**, 1636—1638).—A modification of Bekk's combustion

method (A., 1913, ii, 981) is described. Instead of the large quantity of asbestos impregnated with cerium dioxide, a layer only 3 cm. long is used, followed by a layer of copper oxide, 20 cm. long. This is more satisfactory for the use of students than the original method, but it cannot be employed for the simultaneous estimation of carbon, hydrogen, and halogens. E. G.

Simple Laboratory Apparatus for the Estimation of Carbon Dioxide by Loss. STUART P. MILLER (*J. Amer. Chem. Soc.*, 1915, **37**, 1730).—The apparatus described is simpler and less expensive than the Schrötter form, and gives results with an accuracy of 0·1%. It consists of a small, wide-mouthed flask, fitted with a two-holed cork carrying a thistle funnel and a calcium chloride tube. The mouth of the thistle funnel is closed by a thin cork, through which passes a short piece of glass tubing with a bore only slightly greater than the diameter of a sliding valve-tube which is inserted through it. The valve-tube is closed at each end, and has an inlet hole at a point rather less than half-way down, and a small exit hole nearly at the bottom. A piece of rubber tubing at the lower end of the thistle funnel is employed to seal the exit. Acid is placed in the thistle funnel, the cork is replaced, and the apparatus weighed. The sample to be analysed is introduced into the flask, and the whole is again weighed. On pushing down the valve-tube, the exit hole comes below the rubber tubing, and acid flows into the flask. When the required amount of acid has been allowed to enter the flask, the valve-tube is raised, the exit being thus sealed. The flask is afterwards heated gently, and the valve-tube is pushed down, and air is drawn through the apparatus to remove all the carbon dioxide. When the apparatus has cooled, it is weighed, and the percentage of carbon dioxide calculated from the loss of weight. E. G.

Volumetric Estimation of Potassium in Mineral Waters. L. L. BURGESS and OLIVER KAMM (*Chem. Zentr.*, 1915, i, 398—399; from *Univ. of Illinois Bull.*, 1913, **10**. Compare A., 1912, ii, 604).—The method depends on the precipitation of the potassium as silver potassium cobaltinitrite; in this salt the ratio

$$(Ag+K) : NO = 1 : 1{\cdot}90.$$

The neutral potassium solution, containing a known quantity of, at the most, $N/50$-silver nitrate solution, is added slowly with constant stirring to an excess of 25% sodium cobaltinitrite solution. After thirty minutes the precipitate is collected, washed wi ice-water containing 0·2% of acetic acid, then oxidised with an excess of $N/10$-permanganate solution, the mixture acidified, and the excess of permanganate titrated with oxalic acid solution. The excess of silver in the filtrate is titrated with thiocyanate solution. The presence of sodium, calcium, and magnesium salts, except in large amount, does not interfere with the reaction. The results obtained by the method agree with those obtained by precipitating the potassium with platinum chloride; with quantities of 0·04 gram of potassium, the error varies from $-0{\cdot}0005$ to $+0{\cdot}0012$ gram.

The chlorine in waters should be removed previously by precipitation with silver nitrate, and the quantity of the latter in the filtrate then adjusted before the potassium is precipitated.

W. P. S.

Separation of Potassium and Sodium by the Use of Aniline Perchlorate, and the Subsequent Estimation of Sodium. D. U. HILL (*Amer. J. Sci.*, 1915, [iv], **40**, 75—77).—Mixtures of weighed amounts of sodium and potassium chlorides were dissolved in a small volume of water, and sufficient alcoholic solution of aniline perchlorate was then added, so that a 97% alcoholic solution of the salts was obtained. Potassium perchlorate was precipitated, collected, washed with 97% alcohol, dried at 110°, and weighed. The filtrate was then saturated with hydrogen chloride, whereby the sodium was precipitated as sodium chloride; this was filtered off, washed with a saturated solution of hydrogen chloride in 97% alcohol, dried, and weighed. Working with weights of sodium chloride and potassium chloride of 0·05—0·03 gram each, results were obtained which in the case of potassium showed an error of $-0·0006$ to $+0·0001$ gram K_2O, and in the case of sodium showed an error of from $-0·0004$ to $-0·0002$ gram Na_2O. J. F. S.

Hydrofluoboric and Hydrofluosilicic Acids in the Qualitative Analysis of Sodium. F. C. MATHERS, C. O. STEWART, H. V. HOUSEMANN, and I. E. LEE (*J. Amer. Chem. Soc.*, 1915, **37**, 1515—1517).—The following method is recommended for the qualitative analysis of the metals of the alkali group. After the other metals have been removed in the usual way, the filtrate containing the potassium, sodium, ammonium, and magnesium is evaporated to dryness and ignited to expel the ammonium salts. The residue is dissolved in warm water. The solution is diluted with an equal volume of alcohol, and excess of hydrofluoboric acid in 50% alcohol is added, the potassium being thus precipitated completely as potassium borofluoride. The solution after filtration may contain sodium and magnesium. On adding hydrofluosilicic acid, sodium silicofluoride separates as a gelatinous, semi-transparent precipitate, the magnesium remaining in solution. One mg. of sodium in 5 c.c. of 50% alcohol can be easily detected in this way.

The chief advantages of the method are that tests can be made in presence of magnesium; that the reagents are inexpensive and easily prepared; and that the analysis can be carried out quickly and with trustworthy results. E. G.

Estimation of Very Small Quantities of Lead in Water. HANS PICK (*Chem. Zentr.*, 1914, ii, 1366; from *Arbb. Kaiserl. Gesundh.-Amt.*, 1914. **48**, 155—164).—The method described by Kühn (A., 1906, ii, 493) yields trustworthy results only when certain kinds of asbestos are employed. Iron and manganese do not interfere with the estimation; copper and zinc, when present in quantities not exceeding a few mg. per litre, are without influence except that they increase the time required for the analysis. W. P. S.

Detection and Estimation of Lead in Animal Organs. FAUCONNIER (*Ann. Chim. anal.*, 1915, **20**, 126—127; from *Bull. Soc. pharm. Bordeaux*, 1914).—One hundred grams of the substance are treated with nitric acid containing 10% of sulphuric acid, and, after twenty-four hours, the mixture is heated until a clear solution is obtained. The solution is neutralised with ammonia, a small quantity of hydrochloric acid is added, and the heavy metals are precipitated by hydrogen sulphide. The sulphides are collected, washed, dissolved in nitric acid, and the solution is evaporated to dryness. The residue is dissolved in water, potassium thiocyanate added, and the mixture extracted with ether, which dissolves the ferric thiocyanate. The aqueous portion is then heated to expel ether, cooled, diluted to a definite volume, and the lead estimated colorimetrically as sulphide in the presence of potassium cyanide. The following quantities of lead were found in normal human organs: Liver (weight, 1250 grams), 0·0062 gram; brain (1160 grams), 0·0024 gram; kidney (115 grams), 0·00026 gram; placenta (420 grams), 0·00039 gram. W. P. S.

Analysis and Composition of Red Lead. AUGUSTUS P. WEST (*Chem. Zentr.*, 1914, ii, 508; from *Philippine J. Sci.*, 1914, **8**, 429—437).—Insoluble substances are estimated by heating 2 grams of the sample with 100 c.c. of 10% nitric acid, adding sugar to reduce the lead dioxide, and collecting the insoluble residue on a filter. To estimate the free lead monoxide, 0·5 gram of the sample is extracted with hot 10% lead nitrate solution; this dissolves the free monoxide, and its quantity is found (by difference) by collecting and weighing the insoluble portion. A further quantity of 0·5 gram of the sample is then heated for thirty minutes on a water-bath with 100 c.c. of 10% nitric acid, and the lead dioxide, together with insoluble substances, is collected and weighed; by subtracting the weight of the insoluble substances, the amount of lead dioxide is found. The filtrate is evaporated with sulphuric acid, and the resulting lead sulphate weighed; its quantity is equivalent to the free and combined lead monoxide in the sample. It is shown that red lead does not consist of Pb_3O_4, but is a mixture of Pb_3O_4 and Pb_4O_5. The percentage quantities of Pb_3O_4 and Pb_4O_5 can be calculated from the ratio of lead dioxide to combined lead monoxide. Commercial red lead contains: Free lead monoxide, 5·36—41·36%; Pb_3O_4, 51·85—83·14%; and Pb_4O_5, 6·41—20·37%. W. P. S.

Valuation of Commercial Lead Arsenate. R. H. ROBINSON and H. V. TARTAR (*J. Ind. Eng. Chem.*, 1915, **7**, 499—502).—Water-soluble arsenious oxide and lead oxide are estimated by extracting the sample with hot water, filtering the solution, and titrating an aliquot portion of the filtrate with iodine solution after reduction with potassium iodide; the total soluble impurities are obtained by evaporating a portion of the solution and weighing the residue. The lead hydrogen arsenate is estimated in the portion of the sample insoluble in water by the method described previously by the authors (A., 1914, ii, 773). The quantity of lead carbonate

present is calculated from the amount of carbon dioxide found in the sample. The acid-insoluble substances are estimated by treating 10 grams of the sample with warm 10% nitric acid, collecting the insoluble residue, and weighing it after drying at 110°. Chlorides are estimated by titration with thiocyanate solution, and the presence of acetates may be detected by converting the acetic acid into ethyl acetate and observing the characteristic odour.

W. P. S.

Method of Assaying Copper. ARTHUR FRASER (*J. Soc. Chem. Ind.*, 1915, **34**, 462—464).—A modification of the iodine method is described, the important feature of which is the addition of sodium fluoride, which converts any ferric salt into ferric fluoride, and so prevents any reaction with potassium iodide. Full details are given. The method gives trustworthy results, may be applied to ores containing as little as 0·5% of copper or to samples containing 70% or more, and all the operations may be performed in the one vessel.

J. C. W.

New Test for Copper. W. G. LYLE, L. J. CURTMAN, and J. T. W. MARSHALL (*J. Amer. Chem. Soc.*, 1915, **37**, 1471—1481).—Kober and Sugiura (A., 1913, ii, 990) have suggested that the insoluble complex which α-amino-*n*-hexoic acid forms with copper might prove useful in analytical work, and it has now been found that the reagent is of considerable value as a means of detecting small quantities of copper.

An aqueous solution of α-amino-*n*-hexoic acid is capable of detecting 0·004 mg. of copper. The only other common metals which yield a precipitate with the reagent are mercury and zinc. The interference of the former can be obviated by the addition of sodium chloride, and the precipitation of the latter can be prevented by adjusting the acidity of the solution. Methods are described for applying this test for copper in presence of relatively large quantities of other metals. The test has the advantage over the ferrocyanide test of being applicable in presence of small amounts of iron.

E. G.

Estimation of Aluminium Volumetrically. I. P. OSIPOV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 613—615).—The relative errors obtained in the estimation of aluminium in potash alum by different methods are as follows: Stock (A., 1900, ii, 247, 315), −0·0005 to +0·0006; Moody (A., 1905, ii, 765), −0·0003 to −0·0006; Ivanov (A., 1914, ii, 671), −0·0004 to −0·0015. The results obtained by Kovscharova, in conjunction with the author, are given in the following paper (succeeding abstract).

T. H. P.

Application of Stock's Reaction to the Volumetric Estimation of Aluminium. (Mlle.) T. V. KOVSCHAROVA (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 616—624).—The author has applied Stock's reaction (A., 1900, ii, 247, 315) to the volumetric estimation of aluminium in potash alum. To a definite volume of the alum

solution are added a mixture in equal volumes of 25% potassium iodide and 6% potassium iodate solutions, and an excess of $N/10$-sodium thiosulphate solution. The liquid is then heated to boiling, and the excess of thiosulphate estimated by titration with $N/10$-iodine solution. A large number of estimations, carried out under different conditions, shows that trustworthy results are obtained when (1) the excess of sodium thiosulphate solution taken is small, (2) the solution is as nearly neutral as possible, and (3) the heating on the water-bath is not continued for longer than twenty to thirty minutes. T. H. P.

Detection and Estimation of Manganese in Water. J. TILLMANS and H. MILDNER (*Chem. Zentr.*, 1914, ii, 1249; from *J. Gasbeleucht.*, 1914, **57**, 496—501).—A combination of the method described by Trillat (A., 1903, ii, 512) and Benedict (A., 1906, ii, 128) may be used for the detection of manganese; the water is shaken with solid potassium periodate, acidified with acetic acid, and a solution of tetramethyldiaminodiphenylmethane in chloroform is added. A blue coloration is obtained with as little as 0·05 mg. of manganese per litre. Iron salts should be removed previously by treatment with zinc oxide. The method proposed by Baumert and Holdefleiss (A., 1904, ii, 782) for the estimation of manganese is untrustworthy; Marshall's reaction may be used for the purpose (compare A., 1913, ii, 880). Ten c.c. of the water are heated for twenty minutes with the addition of silver nitrate, nitric acid, and persulphate, and the resulting permanganate is estimated colorimetrically by comparison with permanganate solutions of known strength. The interfering action of iron salts may be prevented by the addition of sodium phosphate. Methods described by Ernyei (A., 1908, ii, 133) and Knorre (A., 1903, ii, 760) may be employed for the estimation of the manganese when the quantity of the latter exceeds 5 mg. per litre of water. W. P. S.

Permanganate Estimation of Iron in Presence of Fluorides. Analysis of Silicates and Carbonates for their Ferrous Iron Content. O. L. BARNEBEY (*J. Amer. Chem. Soc.*, 1915, **37**, 1481—1496).—When ferrous iron in hydrofluoric acid solution is titrated with permanganate, the end-point is unstable. A study has therefore been made of the effect of various reagents in the titration. Satisfactory results can be obtained by the use of N- to $5N$-sulphuric acid in presence of N-hydrofluoric acid. Ferric and magnesium sulphates react with the hydrofluoric acid, and check its influence in the titration. Molybdenum trioxide and titanium dioxide also exert a beneficial effect, but boric acid is the most effective of all the reagents tested. Solutions of ferrous iron containing hydrofluoboric acid are quite stable in presence of air.

A method for estimating ferrous iron in carbonates and silicates is described, which is based on the decomposition of the material with sulphuric (or hydrochloric) and hydrofluoric acids, and the titration of the solution with permanganate in presence of boric acid. If hydrochloric acid is used in decomposing the sample,

solution of manganous sulphate and sulphuric acid is also added before titration in order to prevent the action of the hydrochloric acid on the permanganate (compare A., 1914, ii, 747). E. G.

Estimation of Pyrites in Soils. V. Rodt (*Chem. Zentr.*, 1915, i, 64—65; from *Mitt. Kaiserl. Materialprufgs. Amt.*, 1914, **32**, 431—432).—A portion of the soil is boiled with water, and the soluble iron is estimated. Another portion of the sample is boiled with dilute (1:3) hydrochloric acid, the soluble sulphate is estimated, and the insoluble residue is dried over sulphuric acid, extracted with carbon disulphide, and, after the extracted residue has been freed from carbon disulphide, it is heated with dilute nitric acid and bromine. The solution obtained is diluted to a definite volume, and the iron and sulphuric acid are estimated in aliquot portions. The quantity of pyrites present is calculated from the results obtained. W. P. S.

Analysis of Ferrochrome. H. Schilling (*Chem. Zeit.*, 1915, **39**, 466).—A quantity of 0·5 gram of the finely divided sample is treated with 10 c.c. of concentrated sulphuric acid, and water is added, drop by drop, until the maximum evolution of gas is reached; about 10 c.c. of water are required. When the reaction slackens, 2 drops of hydrofluoric acid are added, and the mixture is heated until solution is complete. The analysis is then carried out according to the method described by Knorre (A., 1904, ii, 92). The treatment with hydrofluoric acid is necessary owing to the fact that the separated silica persistently retains a small quantity of chromium. When it is desired to estimate silica in the sample, the latter is dissolved as described in sulphuric acid with the addition of water, the silica collected and weighed, then treated with hydrofluoric acid, evaporated, and the residue weighed. The difference between the two weights gives the quantity of silica present. W. P. S.

New Method for the Volumetric Estimation of Nickel. Gino Zuccari (*Ann. Chim. Applicata*, 1915, **3**, 277—279).—This method depends on the precipitation of nickel nitroprusside (compare this vol., ii, 68):

$$Na_2Fe(CN)_5NO + NiSO_4 = NiFe(CN)_5NO + Na_2SO_4.$$

The sodium nitroprusside ($+2H_2O$) is employed in the form of $N/2$-solution or of a solution containing 50·771 grams per litre, 1 c.c. of this corresponding with 0·01 gram of nickel. The standard solution is run slowly from a burette into the solution containing the nickel salt, the liquid being kept well stirred with a glass rod. When the precipitate formed assumes a pale ashen colour, a drop of the liquid is filtered and tested with sodium sulphide, which is blackened so long as the precipitation of the nickel is incomplete. When the final point is reached, the sodium sulphide assumes a faint and transient violet colour.

Good results are obtained if attention is given to the following points: (1) The concentration of the nickel in the solution to be

tested should be not less than 1—1·5%. (2) During the titration the liquid should be well shaken, especially towards the end of the reaction. (3) Thin, compact filter-paper should be employed in order to prevent the passage of the nickel nitroprusside, since otherwise a violet coloration will always be obtained. (4) When the titration is finished, it is well to make a further test of the liquid after the lapse of five minutes, since the complete precipitation of the nickel sometimes requires a little time. (5) The titration is best carried out in distinctly acid solution.

The method is applicable to the estimation of nickel in its ordinary salts and in the presence of salts of tervalent iron, zinc, tin, aluminium, lead, manganese, etc. (*loc. cit.*).

Nickel nitroprusside is pale ashen-grey, and is insoluble in acids. When anhydrous, it is dark green, the original colour being gradually restored in moist air. It dissolves very readily in ammonia solution, giving a brownish-yellow liquid. Potassium hydroxide turns it lemon-yellow, and potassium cyanide solution dissolves it.

Cobalt nitroprusside has a red colour and dissolves in acids, but it is insoluble in potassium hydroxide or ammonia solution, so that the latter serves to separate it from the nickel compound (compare Cavalli, A., 1897, ii, 603). Titration with sodium nitroprusside does not give accurate results when applied to the estimation of cobalt, owing to the appreciable solubility of cobalt nitroprusside. T. H. P.

Estimation of Chromium in Leather. Louis E. Levi and Aug. C. Orthmann (*Chem. Zentr.*, 1915, i, 219; from *J. Amer. Leather Chem. Assoc.*, 1914).—The ash obtained from 3 grams of the finely divided leather is fused in an iron crucible with 3 grams of sodium peroxide, and the resulting chromate is estimated volumetrically. When it is desired to estimate iron and aluminium in addition to the chromium, the ash is fused with a mixture consisting of equal quantities of sodium carbonate, potassium carbonate, and anhydrous borax; the fused mass is dissolved in water, the solution acidified with hydrochloric acid, boiled with the addition of ammonium chloride and a slight excess of ammonia, and the precipitate formed separated by filtration. The chromium is then estimated in the filtrate. W. P. S.

Estimation of Uranium and Phosphorus. H. D. Newton and J. L. Hughes (*J. Amer. Chem. Soc.*, 1915, **37**, 1711—1715).—Newton (A., 1908, ii, 538) has shown that iron in solution as ferric sulphate can be estimated by reducing with titanous sulphate, oxidising the excess of the latter with bismuth trioxide, and titrating the filtered solution with 0·1*N*-potassium permanganate.

It has now been found that uranium in solution as uranyl sulphate can be estimated in the same manner, as titanous sulphate readily reduces this salt, and bismuth trioxide does not exert any appreciable oxidising action on the uranous salt.

It is well known that, under suitable conditions, an alkali phosphate can be completely precipitated by excess of uranyl nitrate,

but the employment of this reaction for estimating phosphorus when a separation of ammonium uranyl phosphate is involved is complicated by the difficulty of collecting the very finely divided precipitate. According to the method now described, the ammonium uranyl phosphate is filtered on asbestos felt contained in a platinum cone and previously moistened with 2% ammonium acetate solution. After the precipitate has been washed with 2% ammonium acetate solution, the cone and its contents are transferred to a funnel and the precipitate is dissolved and washed into a flask with 16% sulphuric acid. The solution is then treated with titanous sulphate and bismuth trioxide, and titrated with potassium permanganate in accordance with the method for estimating uranium.

E. G.

Volumetric Estimation of Antimony, particularly the Estimation of Antimony in Antimony Pentasulphide. Utz (*Chem. Zentr.*, 1914, ii, 1470; from *Gummi-Zeit.*, 1914, **29**, 137—139).—Of various methods investigated those described by Schmitz (A., 1914, ii, 300) and by Lehmann and Berdau (A., 1914, ii, 680) are recommended. W. P. S.

The Quality of Platinum Ware. George K. Burgess and P. D. Sale (*J. Washington Acad. Sci.*, 1915, **5**, 378—380; and *J. Ind. Eng. Chem.*, 1915, **7**, 561—564. Compare A., 1914, ii, 585).—The loss of weight of platinum crucibles at high temperatures has been determined with the aid of an electric furnace containing no heated metal parts. At 1200° the loss in weight of practically pure platinum is about 1 mg. per hour per 100 cm.^{2}. For platinum containing 7·5% of rhodium the loss is about 0·5 mg. per hour, whilst the value for platinum containing 2% of iridium was found to be 2·5 mg.

The presence of rhodium or iridium can usually be detected by microscopic examination of a crucible which has been heated, and from this in combination with thermoelectric measurements it is possible to predict the loss of weight of a crucible on heating with a fair degree of accuracy. H. M. D.

Estimation of Platinum and Palladium. A. M. Smoot (*Chem. Zentr.*, 1915, i, 220—221; from *Österr. Zeitsch. Berg. Hüttenwesen*, 1914. **62**, 578—579).—In solutions containing both palladium and platinum, the palladium may be reduced to $PdCl_2$ by repeated evaporation with hydrochloric acid; the platinum is then precipitated, and separated as $(NH_4)_2PtCl_6$, the solution oxidised with nitric acid, and the palladium precipitated as $(NH_4)_2PdCl_6$. Care should be taken in igniting the ammonium compounds; in the case of ammonium platinichloride it is preferable to dissolve the compound in water, acidify the solution with sulphuric acid, precipitate the platinum with hydrogen sulphide, and collect and ignite the platinum sulphide. W. P. S.

Estimation of Palladium and Platinum. H. D. Greenwood (*Chem. Zentr.*, 1915, **i**, 220; from *Eng. and Min. J.*, 1913).—*Palladium*—

A quantity of 0·5 gram of the sample is heated with 10 c.c. of nitric acid, 5 c.c. of hydrochloric acid, and 5 c.c. of water, and the solution then diluted to 100 c.c., and filtered. Any insoluble residue may consist of palladium oxide; it is boiled with 3 c.c. of formic acid and 5 c.c. of water, and the reduced palladium is dissolved as described. The whole solution is then evaporated with the addition of nitric acid to expel hydrochloric acid, the residual solution is diluted to 100 c.c., 25 c.c. of 10% mercuric cyanide solution are added, the mixture is boiled, and, after about eighteen hours, the precipitate is collected, washed with 1% mercuric cyanide solution, and ignited. The ash (palladium oxide) is then boiled with 50 c.c. of 20% formic acid solution, and the palladium collected and weighed. The palladium oxide may also be reduced by heating it in a current of hydrogen. *Platinum.*—One gram of the sample is dissolved in 10 c.c. of nitric acid, 15 c.c. of hydrochloric acid, and 5 c.c. of water, and the nitric acid is expelled by evaporating the solution with the addition of hydrochloric acid. The solution is then diluted, filtered, and any insoluble residue is treated as described under palladium. The whole solution is evaporated to 40 c.c., and treated with 25 c.c. of alcohol and 25 c.c. of saturated ammonium chloride solution. After eighteen hours the precipitate is collected, washed with 20% ammonium chloride solution, ignited, and weighed. If the proportion of palladium in the same is high, a second precipitation of the ammonium platinichloride is necessary. Copper, if present, may be separated from the palladium by precipitating the latter as ammonium palladichloride. W. P. S.

Detection of Methane. II. O. Hauser and H. Herzfeld (*Ber.*, 1915, **48**, 895—896. Compare A., 1913, ii, 77).—A small apparatus, with a simple ozoniser, is described and figured for use in the authors' test. By means of it, 0·02 gram of methane can be detected as formaldehyde in a few minutes. J. C. W.

Detection of Small Quantities of Paraffin Wax in Beeswax, and the Determination of a New Constant for East Indian and European Beeswaxes. M. S. Salamon and W. M. Seaber (*J. Soc Chem. Ind.*, 1915, **34**, 461—462).—One gram of wax is boiled for an hour with 10 c.c. of 0·5*N*-alcoholic potassium hydroxide and 10 c.c. of alcohol, and the solution is then allowed to cool with continual stirring, and the temperature is noted at which a cloudiness appears. For East Indian waxes this point is 56°, whilst for European waxes it is 60°; in both cases the point is very definite and constant. An admixture of as little as 5% of paraffin wax causes a well-defined rise of a few degrees in this temperature, whilst 10% raises the constant some 15°. J. C. W.

Detection of Methyl Alcohol by Dénigès' Method, and the Application of the Method to the Estimation of Methyl Alcohol in Dilute Solutions. Th. von Fellenberg (*Chem. Zentr.*, 1915, i, 765—766; from *Mitt. Lebensmittelunters. Hyg.*, 1915, **6**, 1—24).—The author has investigated the conditions under which

Dénigès' reaction may be used for the estimation of methyl alcohol. The dilute solution containing the methyl alcohol is distilled until 60% of it has passed over into the distillate; in the case of very dilute solutions the distillate is again distilled. When volatile acids or bases are present, sodium hydroxide or sulphuric acid, respectively, must be added to the distillation flask, whilst the presence of aldehydes, terpenes, etc., requires the addition of silver nitrate and sodium hydroxide. If the methyl alcohol is present in combination as pectin volatile substances are removed by distillation with steam, the residue is then decomposed with sodium hydroxide, acidified with sulphuric acid, and distilled. The methyl alcohol is then estimated by mixing 3 c.c. of the distillate with 1 c.c. of alcohol–sulphuric acid (20 c.c. of absolute alcohol and 40 c.c. of concentrated sulphuric acid are diluted with water to 200 c.c.) and 1 c.c. of 5% potassium permanganate solution, and the mixture is shaken for two minutes. One c.c. of 8% oxalic acid solution is now added, followed by 1 c.c. of concentrated sulphuric acid and 5 c.c. of magenta-sulphurous acid reagent. The coloration obtained is compared with that of standards prepared at the same time and containing known quantities of methyl alcohol (from 1 to 5 mg.). W. P. S.

Detection of Methyl Alcohol in Alcoholic Beverages and Pharmaceutical Tinctures. Giambattista Franceschi (*Chem. Zentr.*, 1914, ii, 434—435; from *Giorn. Farm. Chim.*, 1914, **63**, 250—252).—Twenty c.c. of the liquid to be tested are distilled, and 15 c.c. of distillate are collected; this distillate is re-distilled so as to give 8 c.c. of distillate, into which is plunged a glowing copper spiral. The solution is now divided into two portions. One portion is treated with 1 drop of 10% sodium nitroprusside solution and 1 drop of piperidine; a blue coloration indicates the presence of ethyl alcohol. The other portion is boiled for one minute, a drop of phenol is added, and the solution poured on the surface of concentrated sulphuric acid; a red zone develops if the sample contained methyl alcohol. In testing tincture of iodine, 10 c.c. of the sample should be diluted with 30 c.c. of water, filtered, the filtrate decolorised by the addition of thiosulphate solution, and then tested as described. W. P. S.

Detection of Methyl Alcohol in Ethyl Alcohol. Umberto Pazienti (*Ann. Chim. Applicata*, 1915, **3**, 279—281).—This test is based on the red coloration given by formaldehyde with Schryver's reagent, which consists of 2 c.c. of freshly prepared and filtered 1% phenylhydrazine hydrochloride solution, 1 c.c. of freshly prepared potassium ferricyanide solution, and 5 c.c. of concentrated hydrochloric acid (A., 1910, ii, 334). The procedure is as follows: Five c.c. of the alcohol, diluted to 50 c.c., are distilled with 3 grams of sodium persulphate and 10 c.c. of 20% sulphuric acid from a 250 c.c. flask fitted with a ground-glass stopper and connected with a condenser. The distillate is collected in fractions, each of about 2 c.c., and the fifth such fraction tested with Schryver's reagent.

In this way the presence of 1 part of methyl alcohol in 1000 of ethyl alcohol may be detected. If the oxidation products are tested without previous distillation, the limit of sensitiveness is 4% of methyl alcohol. If the coloration obtained is not very distinct, the distillate should be diluted with water and tested again, since the sensitiveness is diminished when much formaldehyde is present. T. H. P.

Estimation of Methyl Alcohol in the Presence of Ethyl Alcohol. W. A. R. Wilks (*Bull. Wellcome Trop. Res. Lab.*, 1914, No. 1, 1—5).—The following modification of the method described by Thorpe and Holmes (T., 1904, **85**, 1) is recommended in order to reduce the correction due to ethyl alcohol as far as is consistent with the complete oxidation of the methyl alcohol. Thirty grams of potassium dichromate dissolved in 150 c.c. of water are placed in the oxidation flask and cooled with a freezing mixture; 50 c.c. of the alcohol solution are then added, followed by the gradual addition of a mixture of 20 c.c. of sulphuric acid and 20 c.c. of water, this mixture having been previously cooled in a freezing mixture. After about eighteen hours' contact, the carbon dioxide formed from the methyl alcohol is collected as described. In these conditions the subtractive correction is 0·0040 gram of carbon dioxide per gram of ethyl alcohol. W. P. S.

Boiling-point Apparatus for the Estimation of Alcohol in Wine. Ph. Malvezin (*Bull. Assoc. Chim. Sucr. Dist.*, 1914, **32**, 104—108).—The apparatus consists of a conical water-bath surrounded by a casing; a side-tube extends through the casing, and a burner, placed under this side-tube, heats the water in the bath. The wine is contained in a conical vessel in the water-bath, and this vessel is provided with a reflux apparatus. Thermometers are fitted in the wine vessel and the water-bath. W. P. S.

Estimation of Glycerol in Wine. Franz Wohack (*Chem. Zentr.*, 1914, ii, 1209—1210; from *Zeitsch. landw. Vers. Wesen. Österr.*, 1914, **17**, 684—697).—The modification of Zeisel's method described by Klemenc for the estimation of methoxyl- and ethoxyl- groups (A., 1913, ii, 733) may be used for the estimation of glycerol in wine. One hundred c.c. of the wine are evaporated to 30 c.c., then diluted to 50 c.c., and 5 c.c. of this solution are used for the estimation. The liberated iodine is dissolved from the decomposition tube by the aid of potassium iodide solution, and then titrated with thiosulphate solution; the small quantity of hydrogen iodide formed is estimated by subsequently titrating the solution with potassium hydroxide solution, using methyl-red as the indicator. The phosphorus used in the process should be treated previously with carbon disulphide, ether, alcohol, and water. W. P. S.

Colorimetric Method for the Estimation of Acids in Wort and Beer. Heinrich Luers (*Chem. Zentr.*, 1914, ii, 735—736; from *Zeitsch. ges. Brauw.*, 1914, **37**, 334—337).—The following method is

proposed with the purpose of eliminating the influence of the colour of wort and beer during their titration with alkali, using phenolphthalein as the indicator. Four glass cylinders are arranged so that numbers 1 and 2 stand directly behind 3 and 4 respectively. Cylinder 1 contains water, 2 a standard colour solution (a solution of an organic colouring substance, of which the tint corresponds with that of a solution containing 11·876 grams of disodium phosphate per litre and treated with phenolphthalein); 3 and 4 each contain 50 c.c. of the liquid to be titrated mixed with 5 c.c. of phenolphthalein solution and 5 c.c. of water respectively. The liquid in 3 is titrated with alkali solution (about the same quantity is added to 4) until the same tint is observed on looking through the two pairs of cylinders. W. P. S.

Physical Chemistry of Foods. I. The Acidity of Wine. Theodor Paul (*Zeitsch. Elektrochem.*, 1915, **21**, 80—89).—It is shown that the titrimetric estimation of free acid in wine is insufficient for the determination of its acid character. Titration gives the free acid content, but does not give the degree of acidity. The degree of acidity is identical with the concentration of the hydrogen ions in the wine. According to Paul and Günther (*Arbeit. K. Gesundheits.-amt.*, 1905, **23**, 1), the degree of acidity of a wine is the figure expressing the number of milligram ions of hydrogen contained in a litre of the wine. The value can be determined by the inversion of sucrose and the hydrolysis of methyl acetate at 76°. From the examination of seventy-nine German wines by this method, it is shown that the degree of acidity and the free acid, as determined by titration, do not run parallel with one another. The degree of acidity decreases but little on diluting a wine with water, and in some cases it even increases to a slight extent. The slight decrease in the acidity is to be explained by the repression of the ionisation of the acid by salts containing the same ion, in the undiluted wine. The deposition of acid salts in wine brings about an increase in the degree of acidity, despite the fact that an acid has been removed; this is to be explained by the effect of salts on the ionisation of the acid. J. F. S.

Applied Microchemistry of Plants. X. The Microchemical Detection of Lapachol. O. Tunmann (*Chem. Zentr.*, 1915, i, 399; from *Apoth. Zeit.*, 1915, **30**, 50—52. Compare A., 1914, ii, 589).—Lapachol may be sublimed from sections of plants containing the substance. The sublimate appears as flat, monoclinic prisms or plates having a chrome-yellow colour. When the sublimate is treated with a small quantity of ammonia, the smaller crystals dissolve to a red solution, whilst the larger crystals form dark red, or almost black, needles; the latter exhibit a copper colour when examined under polarised light. Lapachol may be extracted directly from the plant tissue by means of chloroform or ethyl acetate and crystallised from the solvent, and the position of the substance in the tissue may be localised by treating the latter with ammonia. W. P. S.

Estimation of Acetone in Urine. N. O. ENGFELDT (*Chem. Zentr.*, 1915, i, 574—575; from *Skand. Arch. Physiol.*, 1915, **32**, 253—286).—In the separation of acetone from urine by distillation, the urine must be acidified previously with oxalic, acetic, or phosphoric acid (1%), or with tartaric acid (3%); as the distillation proceeds, water must be added to the flask, drop by drop, to maintain the original volume of the liquid. From 10 to 100 c.c. of the urine, according to the quantity of acetone present, are diluted to 200 c.c., acidified, and distilled for fifteen minutes; under these conditions, phenols and decomposition products of dextrose do not pass over into the distillate, but the latter will contain traces of aldehydic substances and ammonia. The distillate is collected in 50 c.c. of water, treated with 25 c.c. of 25% potassium hydroxide solution and an excess of $N/10$-iodine solution, and, after the mixture has been shaken for ten minutes, the excess of iodine is titrated with thiosulphate solution. W. P. S.

Estimation of Pentoses and Methylpentoses in Wine. SCHAFFER and E. ARBENZ (*Chem. Zentr.*, 1914, ii, 512; from *Mitt. Lebensmitteluntersuch. Hyg.*, 1914, **5**, 161—172).—In natural wines the pentoses (as arabinose) predominate, the methylpentoses (expressed as rhamnose) amounting to only 0·015—0·029%; in the case of wines prepared from grape residues and raisins, the respective quantities of pentoses and methylpentoses are more nearly equal, the ratios of arabinose to rhamnose being always less than 2. Tollens' method may be used for the gravimetric estimation. Two hundred c.c. of the wine (previously fermented if it contains more than 3 grams of reducing sugars per litre) are distilled to a volume of 50 c.c., this residual solution is treated with 29 c.c. of hydrochloric acid (D 1·19), diluted to 100 c.c. with water, and the mixture distilled until 30 c.c. of distillate have been collected. Thirty c.c. of 12% hydrochloric acid are then added, and the distillation continued, and so on, until the total distillate measures 360 c.c. The distillate is now treated with phloroglucinol, and diluted to 400 c.c. with 12% hydrochloric acid; after twelve hours, the precipitate is collected on a filter, and weighed. The filter is then washed with hot 95% alcohol, and again weighed. The difference between the two weights corresponds with the amount of methylpentoses. Pentoses and methylpentoses may also be estimated colorimetrically. One hundred c.c. of the wine (fermented, if necessary) are evaporated to about 33 c.c., and the residual solution is diluted to 50 c.c. and boiled for two hours under a reflux apparatus with the addition of 22 c.c. of hydrochloric acid (D 1·19). The mixture is now diluted to 100 c.c., distilled rapidly, and the distillate diluted to 100 c.c. Five c.c. of this solution are mixed with 0·2 gram of resorcinol and 10 c.c. of concentrated hydrochloric acid; the mixture is heated in a boiling water-bath for ten minutes, and the coloration obtained compared with that of a standard colour solution prepared by dissolving 10 mg. of Benzylbordeaux B. conc. in 950 c.c.; the colour of this solution corresponds with that given by 0·01% of arabinose. Rhamnose is estimated in a

similar way, but vanillin is used in place of resorcinol, and the mixture is heated for five minutes. A standard solution of indigo-carmine or methylene-blue, corresponding with 0·01% of rhamnose, is used for the comparison. W. P. S.

The Tollens-Krüger Method for the Estimation of Pentosans. O. Fallada, E. Stein, and J. Ravnikar (*Chem. Zentr.*, 1914, ii, 435—436; from *Osterrung. Zeitsch. Zucker-Ind.*, 1914, **43**, 425—432).—The authors find that the barbituric acid method (compare A., 1903, ii, 456) is more trustworthy than the phloroglucinol method, especially in cases where sucrose is present. W. P. S.

Colour Reactions of Aldehydes. Detection of Artificial Invert Sugar and Caramel. D. Schenk and H. Burmeister (*Chem. Zeit.*, 1915, **39**, 465—466).—Furfuraldehyde, benzaldehyde, and formaldehyde yield colorations when treated with phenol, resorcinol, guaiacol, pyrogallol, phloroglucinol, thymol, or β-naphthol in the presence of sulphuric acid; the colorations vary from yellow to red and reddish-violet. The reactions between furfuraldehyde and guaiacol (orange-red coloration) or phenol (orange-yellow) afford sensitive tests for artificial invert sugar and caramel, since both these substances contain furfuraldehyde derivatives. For the detection of added invert sugar in honey, etc., the sample is extracted with ether, the ethereal solution mixed with 10 drops of 5% phenol solution (in ether) or 2% guaiacol solution, the mixture allowed to evaporate at the ordinary temperature, and the residue treated with 3 c.c. of concentrated sulphuric acid. The test is stated to be more sensitive than those described by Fiehe (A., 1910, ii, 887) and Litterscheid (A., 1913, ii, 351). The presence of caramel in vinegar, brandy, etc., may be detected in a similar manner, but in the case of alcoholic liquids the alcohol must be expelled by evaporation before the liquid is extracted with ether. W. P. S.

Estimation of Reducing Sugars by Fehling's Solution. Various Sources of Error. H. Pellet (*Ann. Chim. anal.*, 1915, **20**, 123—125).—Pure sucrose reduces Fehling's solution to a slight extent, the amount of cuprous oxide formed depending on the period of boiling, the alkalinity of the solution, and its concentration. Consequently, untrustworthy results may be obtained in the estimation of small quantities of reducing sugars in samples of sucrose. No trace of reduction by sucrose takes place, however, if the sugar solution and the Fehling's solution are heated together at 63° for ten minutes, but reducing sugars, if present, react in the usual way. When the quantity of cuprous oxide produced does not exceed 7 mg., the liquid should be filtered through a disc of filter-paper fixed between two ebonite rings; after washing, the exposed part of the paper will exhibit a more or less red coloration according to the quantity of the cuprous oxide. With larger quantities of cuprous oxide, the ordinary gravimetric process is

employed. The asbestos used in the filter, in this case, should be treated previously with boiling sodium hydroxide solution, and then washed. W. P. S.

Estimation of Sugar in Blood. W. Autenrieth and Wilhelm Montigny (*Chem. Zentr.*, 1915, i, 961 ; from *Münch. med. Woch.*, 1914, **61**, 1671—1674).—A quantity of 2·5 grams of the blood is poured into boiling $N/100$-acetic acid, the mixture filtered (the addition of sodium chloride is sometimes necessary to obtain a coagulum), and the filtrate is evaporated. The residue is extracted with alcohol, the alcoholic solution evaporated, the residue dissolved in 20 c.c. of water, and the solution boiled for four minutes with the addition of 5 c.c. of Lang's solution, 2 grams of potassium thiocyanate, and 2·5 grams of potassium carbonate. The solution is then cooled rapidly, diluted with potassium thiocyanate solution to 50 c.c., and the coloration compared in an Autenrieth-Königsberger colorimeter (A., 1910, ii, 910) with suitable standards. W. P. S.

Estimation of Sucrose by Invertase. H. Pellet (*Ann. Chim. anal.*, 1915, **20**, 121—122).—Methods which have been proposed for the estimation of sucrose, and involving the inversion of this sugar by means of invertase, differ considerably in their procedure; in some cases yeast is employed directly, in others yeast-water, whilst invertase prepared from yeast has been used frequently. The inversion has been carried out at temperatures varying from 15° to 55°, and for periods ranging from a few minutes to several days, and precautions have not been taken to prevent alcoholic fermentation. The author is now investigating a method for the inversion of sucrose by the action of yeast. W. P. S.

Estimation of Indican in Urine. Adolf Jolles (*Zeitsch. physiol. Chem.*, 1915, **94**, 79—103. Compare A., 1913, ii, 892).—The test for indican in urine has been modified as follows: 10 c.c. of urine are shaken with 1 c.c. of a 5% alcoholic solution of thymol. About 10 c.c. of fuming hydrochloric acid containing 5 grams of ferric chloride per litre are added, and the mixture is well shaken and kept for about fifteen minutes. The liquid is then gently shaken with 4 c.c. of chloroform, which, if the urine contains 0·000032% or more of indican, assumes a more or less intense violet colour.

The coloured compound is formed from one mol. of indoxyl and one mol. of thymol with simultaneous oxidation by the ferric chloride. The pure substance crystallises in red prisms, m. p. 218—220° (decomp.), and is believed to be 6-*indoxyl*-1-*methyl*-4-iso*propyl*-$\Delta^{1:4}$-cyclo*hexadien*-3-*one*,

$$C_6H_4\begin{matrix}CO\\NH\end{matrix}>C:C<\begin{matrix}CH:CPr^{\beta}\\CMe:CH\end{matrix}>CO,$$

because on hydrolysis anthranilic acid and probably *p*-thymotinaldehyde are produced. The substance does not dye either mordanted or unmordanted animal or vegetable fibres. It forms a crystalline hydrochloride, containing 1HCl, which dissolves in chloroform, forming a deep violet solution. On shaking with water or very dilute alkali, the free base is liberated, and remains

dissolved in the chloroform, forming a deep red solution, which forms the basis for the following new colorimetric method for the estimation of indican in urine.

The urine is first treated with one-tenth of its volume of lead acetate, and 5—10 c.c. of the filtrate are then shaken with 1 c.c. of a 5% alcoholic solution of thymol and 5—10 c.c. of fuming hydrochloric acid. After two hours the mixture is extracted with small quantities of chloroform, which are then combined and shaken with water to liberate the red base. After diluting the chloroform extract to 50 c.c. its colour is compared with that of a standard solution containing 0·01 gram of the pure base (equivalent to 0·009 gram of indican) in 100 c.c. of chloroform. Using solutions containing known quantities of indican, the author compares this new method with that of Ellinger (A., 1903, ii, 620) with satisfactory results. With pathological urines, however, the results obtained by the two methods are not concordant. Autenrieth and Funk's colorimetric method has also been investigated, and found to give inaccurate results. H. W. B.

Jaffe's Indican Test. M. Rhein (*Chem. Zentr.*, 1915, i, 962; from *Munch. med. Woch.*, 1914, **61**, 1503).—In carrying out this test it is recommended that, in place of calcium hypochlorite solution, "antiformin" should be added to the urine mixed with its own volume of concentrated hydrochloric acid. W. P. S.

Modification of Wichmann's Method for the Detection of Small Amounts of Coumarin, Particularly in Factitious Vanilla. J. R. Dean (*J. Ind. Eng. Chem.*, 1915, **7**, 519).—Wichmann's method (converting the coumarin into salicylic acid by fusion with potassium hydroxide, and identifying the salicylic acid by the ferric chloride test) is modified as follows in order that salicylic acid and "saccharin," if present, shall not interfere with the test. A de-alcoholised portion of the vanilla extract is rendered alkaline with ammonia, and extracted with ether; this solvent removes the coumarin, whilst the salicylic acid, vanillin, and "saccharin" remain in the aqueous solution. The ethereal extract is then evaporated, the residue fused with potassium hydroxide at the lowest possible temperature, cooled, the mass dissolved in water, the solution acidified with sulphuric acid, and extracted with chloroform. The chloroform solution is separated and shaken with 2 c.c. of water and a few drops of ferric chloride solution; a violet coloration denotes the presence of coumarin in the sample.

Attention is drawn to the fact that coumarin would interfere with Durand's test for "saccharin" (A., 1914, ii, 227) unless the coumarin is separated by an immiscible solvent in the presence of ammonia. W. P. S.

Volumetric Estimation of Ferrocyanides. Bertram Campbell (*Analyst*, 1915, **40**, 327—328).—The method consists in titrating the iron after the ferrocyanide has been decomposed with sulphuric

acid and the iron reduced to the ferrous state. About 2 grams of the powdered ferrocyanide are heated with 30 c.c. of sulphuric acid (the concentrated acid diluted with one-fifth of its volume of water) until the cyanogen complex is decomposed. The mixture is then cooled, diluted, 5 grams of zinc are added, and, when the zinc has dissolved, the solution is titrated with permanganate solution. One c.c. of $N/10$-permanganate solution is equivalent to 0·0422 gram of crystallised potassium ferrocyanide, or to 0·0484 gram of crystallised sodium ferrocyanide. A correction must be made for the quantity of permanganate used by the small quantity of iron present in the zinc. The method is trustworthy, the error varying from $-0·1$ to $+0·2\%$, but cannot be used in the case of crude products, since these usually contain complex iron cyanogen compounds other than ferrocyanides. W. P. S.

Estimation of Lactic Acid in Wine. A. Gasparini (*Chem. Zentr.*, 1915, i, 509—510; from *Staz. sperim. agrar. ital.*, 1914, **47**, 752—773).—Fifty c.c. of the wine are distilled with steam until 200 c.c. of distillate have been collected; the residual liquid is then transferred to a basin, 5 c.c. of 10% barium chloride solution are added, and the mixture is neutralised with barium hydroxide solution, using litmus paper as the indicator. After the addition of a further 3 c.c. of barium hydroxide solution, the mixture is acidified with hydrochloric acid, heated for ten minutes on a water-bath, again neutralised, transferred to a graduated cylinder, and diluted to 25 c.c., and 95% alcohol is added in quantity sufficient to make the volume up to 100 c.c. The mixture is filtered, 75 c.c. of the filtrate are evaporated in a platinum basin, the residue is ignited, and the ash titrated. W. P. S.

Teschmacher and Smith's Modification of the Goldenberg Method for the Estimation of Tartaric Acid. F. Perciabosco (*Chem. Zentr.*, 1915, i, 1093; from *Staz. sperim. agrar. ital.*, 1914, **47**, 802—809).—The higher results obtained by Teschmacher and Smith's modification of the Goldenberg method (A., 1908, ii, 237) are probably due to the fact that the calcium carbonate is precipitated in an amorphous form; small quantities of potassium tartrate are liable to be precipitated with the crystallised calcium carbonate and removed with the latter from the solution. W. P. S.

Occurrence and Estimation of Citric Acid in Wine and the Detection of Citric Acid in Milk, Jams, and Fruit Syrups. Rudolf Kunz (*Chem. Zentr.*, 1915, i, 99—100; from *Arch. Chem. Mikrosk.*, 1914).—Stahr's reaction (compare Wöhlk, A., 1902, ii, 364) is recommended for the detection of citric acid; the reaction depends on the formation of a white precipitate of pentabromoacetone when bromine and potassium permanganate act on citric acid. The author prefers to use potassium bromide in place of bromine; 10 c.c. of the solution to be tested are treated with 1 c.c. of sulphuric acid (1:1) and 0·3 c.c. of 37·5% potassium bromide solution; 1 c.c.

of 5% permanganate solution is then added, the mixture heated for five minutes at 45°, and any traces of manganese dioxide are removed by the addition of a drop of ferrous sulphate solution containing sulphuric acid. A distinct turbidity is obtained with 1 mg. of citric acid. Wines usually give a precipitate with bromine alone, and in this case the test is modified by evaporating 50 c.c. of the wine to 10 c.c., adding 2 c.c. of dilute sulphuric acid, then 10 c.c. or more of saturated bromine water, diluting the mixture to 50 c.c., and filtering it through kieselguhr. The filtrate is then tested as described. Red and white wines examined all yielded a reaction for citric acid, although the quantity present was usually very small. Using a larger quantity of the wine (100 c.c.), the pentabromoacetone formed may be collected, dried over sulphuric acid, then washed with very dilute sulphuric acid, again dried, and weighed.

For the detection of citric acid in milk, the latter is warmed with dilute sulphuric acid, the serum treated with tannin to remove soluble proteins, filtered, and the test applied to the filtrate. Fresh milk appears to contain more citric acid than does old and curdled milk. In the case of jams, a portion of the sample is diluted with water, acidified with a few drops of sulphuric acid, the solution is mixed with about twice its volume of alcohol, and filtered. The filtrate is neutralised with ammonia, evaporated to expel alcohol, again filtered after the addition of dilute sulphuric acid, and the filtrate used for the test. If the filtrate gives a precipitate with bromine, it is treated as described under wine. Fruit juices also require a similar treatment before being tested.

W. P. S.

Occurrence of Citric Acid in Pressed Yeast. Rudolf Kunz (*Chem. Zentr.*, 1915, i, 101; from *Arch. Chem. Mikrosk.*, 1914).—The citric acid may be isolated as follows: Two hundred and fifty grams of the yeast are digested with 500 c.c. of cold alcohol for two days, then filtered, the filtrate is treated with a slight excess of ammonia, and boiled under a reflux apparatus for twenty minutes. After cooling, the solution is neutralised with hydrochloric acid, calcium chloride is added, the precipitate collected, and boiled with sodium carbonate solution; the resulting sodium citrate is again precipitated as calcium citrate; this is decomposed with sulphuric acid, the calcium sulphate separated, and the citric acid crystallised from the solution. It may be identified by means of Stahr's reaction (preceding abstract). The quantity of citric acid in pressed yeast varies with the kind of yeast; bottom fermentation yeast is free from the acid. W. P. S.

Estimation of Hippuric and Benzoic Acids in Blood and Tissue. F. B. Kingsbury (*J. Biol. Chem.*, 1915, **21**, 289–295).—The method is based on that of Folin and Flanders; preliminary removal of proteins is effected by tannic acid. W. D. H.

Estimation of Salicyluric Acid. Alessandro Baldoni (*Chem. Zentr.*, 1915, i, 169; from *Arch. Farm. sperim.*, 1914, **18**, 1—8).—The slight solubility of salicyluric acid in chloroform affords a

means of separating this acid from salicylic acid; 20 c.c. of chloroform dissolve 0·2 gram of salicylic acid, but only 0·01 gram of salicyluric acid. The solubility of salicyluric acid is diminished when salicylic acid is also present. For the estimation of salicyluric acid in urine, the latter is evaporated to a syrup, acidified with sulphuric acid, and extracted with ether; the residue obtained on evaporating the ethereal solution is dissolved in a small quantity of hot water, the solution is treated with blood-charcoal, filtered, and the filtrate, measuring not more than 50 c.c., extracted with 150 c.c. of chloroform. When more than 0·5 gram of salicyluric acid is present it may separate as crystals from the aqueous solution when this is shaken with chloroform. The chloroform solution is then separated, and the salicyluric acid extracted from the aqueous solution with ether. W. P. S.

Estimation of Urinary Acidity. J. CLARENS (*Compt. rend.*, 1915, **160**, 814—817).—In order to obtain a true measure of the acidity of a sample of urine, the author considers that the following method should be used instead of the usual simple titration with $N/10$-sodium hydroxide. A definite volume of the urine is heated to the boiling point with a known volume of $N/10$-hydrochloric acid, then quickly cooled, and when cold titrated with $N/10$-sodium or potassium hydroxide, using phenolphthalein as indicator. The volume of alkali required minus the volume of acid used is a measure of the acidity. If the result is negative, the urine is alkaline. In using this method care must be taken that the boiling with the acid is not prolonged, and the titration with the alkali must be performed in the cold. If, during the boiling with the acid, a pale pink colour appears, the liquid must be diluted with recently boiled, distilled water before the titration is performed. W. G.

Estimation of Uric Acid in Blood, using 0·1 c.c. of Blood Serum. TH. BRUGSCH and L. KRISTELLER (*Chem. Zentr.*, 1915, i, 1090; from *Deutsch. med. Woch.*, 1914, **40**, 746—747).—About 20 drops of the blood are placed in a small tube, and, after three hours, 0·1 c.c. of the clear serum is transferred to a test-tube and treated with 2 c.c. of 7·5% sodium carbonate solution and 0·4 c.c. of phosphotungstic acid reagent (prepared by boiling a mixture of 100 grams of sodium tungstate, 80 c.c. of 85% phosphoric acid, and 700 c.c. of water for several hours, and then diluting it to 1 litre). A blue coloration is developed, the intensity of which is proportional to the quantity of uric acid present. After five minutes the colour is compared with an empirical graduated scale. W. P. S.

Estimation of Uric Acid in Blood and Urine. W. AUTENRIETH and A. FUNK (*Chem. Zentr.*, 1915, i, 918; from *Munch. med. Woch.*, 1914, **61**, 457—461).—A method described is based on the action of uric acid on iodic acid; an equivalent quantity of the latter is reduced to hydrogen iodide, and this reacts with the excess of iodic acid and liberates iodine. The iodine is dissolved in chloro-

form, and estimated by comparison in the Autenrieth-Königsberger colorimeter (A., 1910, ii, 910). The method is particularly useful for the estimation of uric acid in urine, but the uric acid must first be precipitated as ammonium urate in order to eliminate the thiocyanates present in normal urine; carbamide, creatine, creatinine, hippuric acid, benzoic acid, dextrose, alloxan, and allantoin do not interfere with the reaction. When great accuracy is required, mucoid substances should also be removed previous to estimating the uric acid. The method may also be used for the estimation of uric acid in blood when the latter contains not less than 4 mg. per 100 c.c.; proteins are first removed from the blood as described by Folin and Denis (*J. Biol. Chem.*, 1913, **13**, 467). For very small quantities of uric acid, the phosphotungstic acid method (A., 1913, ii, 444) is recommended. W. P. S.

Estimation of Uric Acid in Urine. M. Bernard (*Chem. Zentr.*, 1914, ii, 957; from *Apoth. Zeit.*, 1914, **29**, 715—716).—One hundred c.c. of the urine, previously freed from albumin, are treated with 4 grams of ammonium chloride, and, after three hours, the precipitate formed is collected on a filter and washed with hot 96% alcohol. The precipitate is then dissolved off the filter with 30 c.c. of hot *N*/10-potassium hydroxide solution, the filter is washed with hot water, the solution boiled until the vapours no longer turn red litmus paper blue, cooled, and the excess of alkali titrated with *N*/10-acid, using phenolphthalein as the indicator. The results obtained agree with those found by the Ludwig-Salkowski method. W. P. S.

Estimation of the Oxyproteic Acid Fraction in the Urine. Otto von Fürth (*Biochem. Zeitsch.*, 1915, **69**, 448—460).—The author has improved the method of Sassa. The urea of the urine is first destroyed by Soja-urease, and the ammonium carbonate is then converted into the sulphate, the greater part of which is precipitated from the faintly acid solution by 95% alcohol; the remainder is then destroyed with barium hydroxide, the excess of which is precipitated by carbon dioxide. The filtrate is evaporated to dryness with kieselguhr, and the alcohol-soluble substances are extracted from the residue by hot alcohol. A water-soluble, alcohol-insoluble fraction of barium salts ("baryta fraction") is thereby obtained, in which the nitrogen is estimated. From this, the oxyproteic acid fraction is precipitated by mercuric acetate and sodium carbonate, and in this the nitrogen is also estimated. For normal human urine, about 4·8% of the nitrogen is contained in the baryta fraction, and a mean of 3·1% in the oxyproteic acid fraction. These numbers are higher than those found by Sassa, owing possibly to the hydrolytic action of the Soja-urease and the barium hydroxide employed by the author. S. B. S.

Estimation of the Amino-acids of Food-stuffs by the Van Slyke Method. H. S. Grindley, W. E Joseph, and M. E. Slater (*J. Amer. Chem. Soc.*, 1915, **37**, 1778—1781).—**The nutritive values of the**

mixed proteins of food-stuffs depend ultimately on the amino-acids they contain, rather than on the proportions of the various proteins. The authors have therefore applied Van Slyke's method of estimating the different amino-acids of proteins (A., 1910, ii, 751; 1911, ii, 779; 1913, ii, 1084) to the direct estimation of such acids in food-stuffs. The results of the estimation of the various amino-acids of cotton-seed meal, tankage, and lucerne hay indicate marked differences in the quantities of these acids in the three materials.

E. G.

Reaction of Hexamethylenetetramine. SIEGFRIED GROSS (*Chem. Zentr.*, 1915, i, 1095; from *Wien. klin. Woch.*, 1914, **27**, 755—756).—The urine is mixed with one-third of its volume of 10% acetic acid, and 7% mercuric chloride solution is added, drop by drop, as long as the turbidity which forms increases in intensity. The urine should be freed from albumin before the test is made, but small quantities of albumin do not interfere, as it is easy to distinguish the heavy precipitate produced by hexamethylenetetramine from the turbidity due to albumin. W. P. S.

Analysis of Urine. Possibility of Mistaking Hexamethylenetetramine for Albumin. J. SCHUMACHER (*Chem. Zentr.*, 1915, i, 1095; from *Deutsch. med. Woch.*, 1914, **40**, 1523—1524).—The reaction between potassium picrate and hexamethylenetetramine described by Schmiz (A., 1914, ii, 309) is not characteristic of the latter substance; the compound formed is an aminophenol, and results from the reduction of the picrate. In the case in question, formaldehyde is the reducing agent, but other substances, such as dextrose, etc., give the reaction. In the estimation of sugar in urine by Fehling's method, attention should be paid to the possible presence of hexamethylenetetramine derivatives. W. P. S.

Estimation of Urea in Urine. A. HAHN and I. SAPHRA (*Chem. Zentr.*, 1915, i, 1094; from *Deutsch. med. Woch.*, 1914, **40**, 430—431).—The method proposed depends on the conversion of the urea into ammonium carbonate by the action of urease; this enzyme may be prepared as a dry product by precipitating it with alcohol from an acid aqueous extract of soja beans. One c.c. of the urine is placed in a 50 c c flask, and 10 c.c. of water, a small quantity of the dry enzyme and 5 drops of toluene are added; a similar mixture, but without the enzyme, is placed in a second flask. The flasks are closed with corks, and, after twenty hours, the contents are titrated with $N/10$-hydrochloric acid, using methyl-orange as the indicator. The difference in the number of c.c. of $N/10$-acid required for the two titrations is multiplied by 0·003 to obtain the quantity of urea in 1 c.c. of the urine. W. P. S.

Estimation of Carbamide in Small Quantities of Blood. L. KRISTELLER (*Chem. Zentr.*, 1914, ii, 1288—1289; from *Zeitsch. exper. Path. Ther.*, 1914, **16**, 496—497).—A quantity of 0·1 c.c. of the blood serum is treated with 1 c.c. of water and 0·4 c.c. of a 1% soja-

urease solution; the carbamide is thus converted into ammonia in thirty minutes. The mixture is then diluted with 15 c.c. of water, 1 c.c. of Nessler reagent is added, and the coloration compared with that shown by a mixture consisting of 0·1 c.c. of serum, 0·1 c.c. of ammonium chloride solution (containing 76·4 mg. of ammonium chloride per 100 c.c.), 16·3 c.c. of water, and 1 c.c. of Nessler reagent. These dilutions are suitable only for quantities of carbamide up to 100 mg. per 100 c.c. of serum. W. P. S.

New Silicotungstic Acid Method for the Estimation of Alkaloids. Aron Ferencz and Ludwig Dávid (*Chem. Zentr.*, 1914, ii, 807; from *Pharm. Post.*, 1914, **47**, 559—563).—Ten c.c. of a solution containing the alkaloid salt are treated with 5 c.c. of 10% silicotungstic acid solution; the precipitate is collected on a filter, and washed with 10 c.c. of very dilute hydrochloric acid. The precipitate is then transferred to a flask, and shaken for five minutes with 5 c.c. of water and 10 c.c. of 20% sodium hydroxide solution; after the addition of 15 grams of sodium chloride and 100 c.c. of ether (in the case of nicotine 50 c.c. of a mixture of ether and light petroleum are used), the mixture is shaken for ten minutes, allowed to separate, and one-half of the ethereal solution is drawn off and titrated with $N/100$-hydrochloric acid, using iodoeosin as the indicator. W. P. S.

Estimation of Caffeine and Antipyrine in Admixture. W. O. Emery and S. Palkin (*J. Ind. Eng. Chem.*, 1915, **7**, 519—521).—The method depends on the conversion of the antipyrine into iodoantipyrine (compare A., 1914, ii, 825), and the subsequent estimation of the iodine in the latter compound. A quantity of 0·25 gram of the caffeine-antipyrine mixture (when these are mixed with the usual excipients in pills and tablets, the sample is extracted with chloroform, and the residue obtained on evaporating the solvent is used for the estimation) is treated in a separating funnel with 10 c.c. of alcohol-free chloroform, 10 c.c. of water, and 1 gram of sodium hydrogen carbonate, and 15 c.c., or more, of $N/5$-iodine solution are added in small quantities at a time. The excess of iodine is then destroyed by the addition of a crystal of sodium thiosulphate, the mixture is extracted with several successive portions of chloroform, the chloroform solution evaporated, and the residue dried at 105°, and weighed. This residue, consisting of iodoantipyrine and caffeine, is dissolved in 5 c.c. of glacial acetic acid, 10 c.c. of saturated sulphur dioxide solution are added, the solution is diluted to 200 c.c., and treated with silver nitrate; after the addition of nitric acid, the silver iodide is collected, dried, and weighed. The weight of the silver iodide multiplied by 0·8012 gives the weight of the antipyrine present; the silver iodide multiplied by 1·3374 gives the weight of the iodoantipyrine, and the amount of the caffeine is obtained by subtracting this weight from that of the residue containing the iodoantipyrine and the caffeine. The method yields trustworthy results. W. P. S.

Estimation of Hydrastine in Plants and in Extracts of Hydrastis Canadensis by the Methods Prescribed in the Various Pharmacopœias, and a New Method for the Estimation of Berberine in Extracts. L. DÁVID (*Chem. Zentr.*, 1915, i, 276; from *Pharm. Post.*, 1915, **48**, 1—4).—The author has determined the solubility of hydrastine in various solvents; 1 gram of the substance is dissolved by 227·27 grams of ether at 20°, by 22727·27 grams of light petroleum (b. p. 40—60°) at 15°, by 11627·88 grams of light petroleum (b. p. 50—85°) at 15°, and by 17·91 grams of benzene at 15°. Hydrastine is soluble in chloroform. The methods given in the German and Belgian pharmacopœias are the most trustworthy for the estimation of hydrastine; then follows that of the Austrian pharmacopœia, whilst the French, Dutch, Swiss, and U.S.A. methods are untrustworthy, as the hydrastine obtained by their use is very impure. The U.S.A. method may be improved by removing the alcohol before the hydrastine is extracted with ether. In the estimation of hydrastine, alcohol must be removed previously, berberine should be separated by precipitation with potassium iodide or hydrochloric acid, and the ethereal extract must be mixed with light petroleum, and the mixed solution treated with tragacanth. A method proposed for the estimation of berberine in hydrastine extracts depends on the precipitation of berberine and hydrastine by potassium bismuth iodide, and the separation of the hydrastine by extraction with ethyl acetate. The precipitate is then treated with 10% sodium hydroxide solution, and the berberine extracted with a mixture of equal parts of ether and chloroform. W. P. S.

Microchemical Detection of Hydrastine and Berberine in Plants. ADOLF MAYRHOFER (*Chem. Zentr.*, 1914, ii, 736—737; from *Pharm. Post.*, 1914, **47**, 547—551).—Picrolonic acid is a suitable reagent for the detection of these alkaloids, crystals being obtained in the following dilutions: Hydrastine hydrochloride, 1 in 15,000; berberine sulphate, 1 in 30,000; and hydrastinine hydrochloride, 1 in 500. The crystals obtained by warming a drop of hydrastine hydrochloride solution with a drop of picrolonic acid solution are bright yellow in colour, but the smallest crystals may be colourless; the crystals are needle-shaped, and may form crosses, stars, etc. The crystals obtained with berberine sulphate under similar conditions appear as bright yellow clusters, whilst hydrastinine hydrochloride yields star-shaped crystals with long, thin threads. For the detection of the alkaloids in plant sections, the section should be treated with a mixture consisting of 2 parts of saturated picrolonic acid solution, 1 part of glycerol, and 1 part of alcohol, and the crystals which form are then identified by treatment with iodine tincture mixed with an equal volume of glycerol. The berberine picrolonate crystals are coloured brown or black, whilst hydrastine picrolonate crystals are not altered. Under the fluorescence-microscope the hydrastine crystals exhibit a white or violet colour, whilst the berberine crystals are yellow. W. P. S.

Estimation of Small Quantities of Heroine. REGINALD MILLER (*Amer. J. Pharm.*, 1915, **87**, 248—250).—Small quantities of heroine in admixture with cocaine and lactose may be estimated as follows. The heroine and cocaine are extracted with an immiscible solvent, and the residue containing the two substances is weighed; it is then dissolved in a definite volume of 1% sulphuric acid, so that 1 c.c. of the solution will contain from 0·01 to 0·05 grain of heroine, and 1 c.c. of this solution is treated with 3 c.c. of a reagent consisting of a mixture of 600 c.c. of commercial sulphuric acid, 300 c.c. of water, and 25 c.c. of 40% formaldehyde solution. After ten minutes, the coloration (yellow to cherry-red) is compared with that produced under similar conditions by known quantities of heroine. W. P. S.

Picramic Acid as a Reagent for Protein Compounds. I. I. OSTROMISSLENSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 317—318).—Addition of finely powdered picramic acid at the ordinary temperature to an aqueous solution or emulsion of pure peptone, albumose, protein, albumin of hen's eggs (puriss.), or the soluble or insoluble globulin of the blood-serum of the horse produces an intense, dark red coloration. If the concentration of the protein compound is very low, or if the solution is coloured, control tests must be made. The solution should be free from alkali and from salts of acids which displace picramic acid. T. H. P.

Colorimetric Estimation of Uric Acid in Urine. STANLEY R. BENEDICT and ETHEL H. HITCHCOCK (*J. Biol. Chem.*, 1915, **20**, 619—627).—Certain changes in the technique proposed in the Folin-Denis method are described, with full details; these greatly improve the accuracy of the method. W. D. H.

Colorimetric Estimation of Uric Acid in Blood. STANLEY R. BENEDICT (*J. Biol. Chem.*, 1915, **20**, 629—631).—After removal of the proteins by colloidal iron, the procedure recommended for the urine can be applied with certain modifications to blood also. W. D. H.

Nephelometric Estimation of Purine Bases and Uric Acid in Blood and Urine. SARA STOWELL GRAVES and PHILIP ADOLF KOBER (*Proc. Amer. Soc. Biol. Chem*, 1914; *J. Biol Chem.*, 1915, **20**, xx).—Salkowski's reagent was modified to suit nephelometric conditions, and a protective colloid (clear egg albumin) introduced. The uric acid and purine bases can be accurately estimated by the method in the urine, and also in the blood, after the proteins are removed by sulphosalicylic acid, followed by talcum powder. Manganese dioxide is excellent for removing alkaline sulphides, and in alkaline suspension will oxidise uric acid completely in three minutes, leaving the other purines intact. W. D. H.

The Use of β-Naphthalenesulphonyl Chloride for the Recognition of Partial Hydrolysis of Flesh-protein. WALTHER LÖB (*Chem. Zeit.*, 1915, **39**, 369—370).—The author confirms

the usefulness of this reagent (compare A., 1914, ii, 443) for detecting the degree of hydrolysis which has taken place in flesh and meat extracts. The method is particularly useful for ascertaining the freshness of various meats, etc. An extract prepared from fresh autolysed flesh or extract is heated with the addition of sodium chloride and acetic acid, filtered, and treated with the reagent; the precipitate is collected, dissolved in sodium hydroxide solution, and the nitrogen estimated in an aliquot portion of the solution by Kjeldahl's method. Fresh flesh yields about 0·04 gram of nitrogen per 250 grams of flesh, and this quantity increases as the flesh hydrolyses with age. W. P. S.

Estimation of Pepsin. L. J. GESELSCHAP (*Zeitsch. physiol. Chem.* 1915, **94**, 205—226).—The amount of pepsin in gastric juice may be estimated with tolerable accuracy by either Mett's or Grützner's method, using a standard pepsin solution for comparison. Three methods are given for preparing pure pepsin from pig's gastric mucous membrane, the products having practically identical proteolytic power, and maintaining their activity unimpaired for several months. When a gastric juice contains a relatively small quantity of pepsin, it is advisable to employ Grützner's method for its estimation. H. W. B.

Rapid Detection and Estimation of Small Amounts of Esterase. A. BACH (*Chem. Zentr.*, 1915, i, 961—962; from *Fermentforschung*, **1**, 151—154).—The method is based on the results of experiments on tyrosinase (A., 1914, i, 445). Phenolase or peroxydase + hydrogen peroxide does not attack undecomposed phenolic esters, but produces pigmented substances when even a trace of esterase is present. Guaiacol carbonate is a phenolic ester particularly suited for the colorimetric estimation.

Fresh fungus juice (from *Lactarius vellereus*) rich in oxydase oxidises guaiacol carbonate directly, whilst the phenolase precipitated therefrom by alcohol is without any action. The fresh juice therefore contains esterase. In the dog the liver is the organ richest in esterase. C. S.

Method for the Estimation of Tobacco Resin, and its Application to Various Tobaccos. JOSEF VON DEGRAZIA (*Chem. Zentr.*, 1915, i, 808—809; from *Fachliche Mitt. der österreichischen Tabakregie*, 1914, 1—4. Compare A., 1914, i, 974).—Two portions of 60 grams each of the dry powdered tobacco are extracted in a Soxhlet apparatus with ether, about 100 grams of ether being used for each portion. One of the ethereal solutions is then washed with water containing a small quantity of acid to remove nicotine, the ether evaporated, the residue dissolved in 90% alcohol, and the solution strongly cooled. After the separated wax has been removed, the alcoholic solution is boiled with the addition of 150 c.c. of 2% potassium hydroxide solution, and the mixture is extracted with ether; the ethereal solution contains the tobacco resin, together with small quantities of ethereal oils. The solution usually has a reddish-brown colour, but in the case of Cserbel

tobacco it has a green colour. After the ether has been evaporated, the residue of tobacco resin is weighed. The alkaline solution contains the resin acids and the resin alcohol; the latter is in suspension, and is separated and weighed, whilst the resin acids are separated by extraction with ether in the usual way, the ethereal solution evaporated, the residue weighed, the acids dissolved in alcohol, and the tobaccic acid precipitated by the addition of alcoholic lead acetate solution. The lead salt is separated by filtration, and the filtrate mixed with ten times its volume of water acidified with nitric acid; the β-tobaccic acid which separates in flocks is collected, dissolved in ether, the solution evaporated, and the residue weighed. The γ-tobaccic acid is found by difference. The other portion of the ethereal solution is evaporated, and the residue extracted with alcohol to dissolve the α-tobaccic acid; the alcoholic solution, which contains tannin and nicotine in addition to the acid, is evaporated, the residue heated with very dilute potassium hydroxide solution, cooled, filtered, the filtrate neutralised, and the separated α-acid collected. The following table shows the composition of the resins from various tobaccos expressed as percentages of the latter; the figures indicate that it is possible to differentiate between different kinds of tobacco:

Kind of tobacco.	Total resin.	Wax.	Resen.	Acids. α.	Acids. β.	Acids. γ.	Resin alcohol.
Havana	4·65	0·59	2·64	1·44	0·18	9·38	0·01
Brazilian	3·36	9·55	1·97	0·93	0·12	0·32	0·02
Java	4·45	0·55	1·37	0·96	0·27	1·75	0·10
Virginian	7·59	0·77	5·75	0·86	0·43	0·44	0·02
Hungarian	5·15	1·32	3·41	0·83	0·24	0·65	0·02
Cserbel (*Nicotiana rustica*)	4·57	0·69	3·46	1·04	0·03	0·04	none
Dalmatian	7·86	1·48	5·88	1·22	0·26	0·45	0·05
Turkish	7·00	1·00	3·80	2·02	0·32	0·81	0·07

W. P. S.

Estimation of Ash in White Bread. J. D. Filippo and W. Adriani (*Chem. Weekblad*, 1915, **12**, 570—576).—From the results of a number of estimations of ash in white bread the authors draw the conclusion that misleading values are given by the ordinary methods for estimating ash and chlorine, even when the charcoal is lixiviated repeatedly with water. There is a tendency for sodium chloride to volatilise, and also to be transformed into sodium carbonate, an error being thus introduced into the chlorine estimation. The improved sulphate method is recommended for estimating the ash in bread, and in other food-stuffs rich in common salt. The estimation of sodium chloride in bread is best effected in the calcium ash by Volhard's method. A. J. W.

General and Physical Chemistry.

New Relations Serving for the Calculation of the Molecular Vibratory Motion of Solids. STEFANO PAGLIANI (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 948—954.* Compare *ibid.*, 835).—The author shows that, for potassium chloride, bromide, and iodide, the vibration frequency, ν, of the compound may be calculated from those of the component elements, ν_1 and ν_2, by means of the expression $\nu/(\nu_1+\nu_2)=4/3$ (1). Thus, the sum of the frequencies of the components is the arithmetic mean between the frequency of the compound and that differing from it by an octave. It is further shown that, for sodium chloride and potassium chloride and bromide, the molecular vibration frequency is connected with the entropy, S_1, by the relation $\nu=9{\cdot}6\,.\,10^{12}S_1$ (2). The successive columns in the following table give the values of ν, (1) deduced from the optical measurements of Rubens and Hollnagel (A., 1910, ii, 172), (2) calculated from Lindemann's formula,

$$\nu=4{\cdot}23\,.\,10^{12}\sqrt{(T_f/MV^{\frac{2}{3}})},$$

(3) assumed in the verification of the Nernst and Lindemann specific heat formula, and (4) and (5), calculated by means of the author's expressions (1) and (2) (*vide supra*):

	(1).	(2).	(3).	(4).	(5).
NaCl	5·9	6·0	5·9	6·1	6·6
KCl	4·5	4·7	4·4	4·4	4·8
KBr	3·6	3·5	3·6	3·7	3·3

Thus, for these salts, just as for the elements, the values of the molecular vibration frequency, like those of the entropy, diminish as the molecular coefficient increases. The coefficient of proportionality between frequency and entropy is equal to that found in the case of the halogens. T. H. P.

Bohr's Theory of the Series Spectra of Hydrogen and Helium. EDWARD RIECKE (*Physikal. Zeitsch.*, 1915, **16**, 222—226).—An account is given of Bohr's theory (A., 1913, ii, 689, 943, 1045) and its application to the series spectra of hydrogen and helium. H. M. D.

Quantitative Absorption Spectra. I. The Chemical Significance of Absorption Spectra and the Methods of Examining Them. FREDERICK RUSSELL LANKSHEAR (*Mem. Manchester Phil. Soc.*, 1915, **58**, No. 15, 1—12).—An account of the methods employed in the investigation of ultra-violet absorption spectra, with special reference to the measurement of extinction coefficients. H. M. D.

The Relation between the Infra-red and Ultra-violet Absorption and the Variation of Absorption with Concentration. EDWARD CHARLES CYRIL BALY and FREDERICK GERALD TRYHORN (T., 1915, **107**, 1121—1132).—It is well known that the effect of a

* and *Gazzetta*, 1915, **45**, ii, 59–66.

solvent on a substance which exhibits selective absorption is to displace the position of the absorption band to a greater or less extent. Quantitative measurements have been made in order to determine the relations which are involved in this displacement.

From observations made with ethyl alcoholic solutions of salicylaldehyde and aqueous solutions of pyridine of widely varying concentration, it has been found that the addition of gradually increasing quantities of solvent results at first in the displacement of the absorption band towards the visible region until a minimum frequency is obtained, which depends on the affinity between solute and solvent. On further dilution, the centre of the band is shifted progressively in the opposite direction until, at great dilution, a maximum frequency is reached. It is shown that this maximum limiting frequency is identical with the frequency of the absorption band found by the investigation of the substance in vapour form.

In addition to this displacement, the addition of increasing quantities of solvent is accompanied by an increase in the absorptive power up to a constant maximum. This is said to be contrary to the requirements of the law of mass action, and an empirical formula is given which is found to satisfy the observed results. If k is the absorption constant corresponding with dilution V, and K the maximum value of k corresponding with the absorption in very dilute solution, the formula may be written $K/K-k=e^{\alpha/V^n}$, where α is a constant which depends on the solute and solvent, and n is the number of entities which are produced from one molecule of the selectively absorbing substance. It is shown, further, that the experimental observations with benzaldehyde, salicylaldehyde, pyridine, and aniline afford further confirmation of the view that the central frequencies of all absorption bands in the ultra-violet and visible regions are integral multiples of a fundamental frequency in the short wave ultra-red. The observed displacements of the ultra-violet bands by the action of solvents are supposed to be dependent on the shift of this fundamental frequency.

H. M. D.

Absorption Spectra of Mono-substituted Benzene Compounds and the Benzene Substitution Law. Edward Charles Cyril Baly and Frederick Gerald Tryhorn (T., 1915, **107**, 1058—1070).—It has been previously noted that there is, in general, a difference between the absorption spectra of those mono-substituted benzene compounds which give meta-disubstitution products and of those which give ortho and para derivatives (Baly and Collie, T., 1905, **87**, 1332). In terms of the theory that the reactivity of a substance depends on the condition of the molecular force fields, by which the character of the ultra-violet absorption is also determined, the authors put forward the view that the nature of the disubstitution products of benzene may be foretold when the absorption spectra of the mono-substituted derivatives have been observed. When the mono-derivative shows a deep and well-developed absorption band, there is but little tendency towards

the closing up of the force field, and the reactivity will be most pronounced in the para-position, with the result that a para-compound will be formed. If, on the other hand, the mono-derivative exhibits an absorption band of small persistence, indicating the existence of a closed field, it will tend to form meta-compounds.

In support of these views, the absorption curves of some twenty-two mono-substituted benzene derivatives have been determined, each of these being examined in the form of a thin film of the pure substance. With three exceptions (benzyl ethyl ether, ethyl phenylacetate, and benzonitrile), the curves plotted from the extinction measurements are in agreement with the deductions made from the force-field theory, for all the compounds which give meta-derivatives show absorption bands of very small persistence, whilst those which form ortho- and para-derivatives all show bands of large persistence.

With regard to the three exceptions, it is pointed out that benzyl ethyl ether and ethyl phenylacetate show no evidence of any absorption band, and the reactivity of these compounds appears also to be very small. On the other hand, benzonitrile would seem to be an undoubted exception, for it shows a band of considerable persistence, and yet chlorine seems to have no action on the substance. H. M. D.

Absorption Spectra of Various Derivatives of Benzoic Acid. JOHN EDWARD PURVIS (T., 1915, **107**, 966—973).—The absorption spectra of alcoholic solutions of derivatives of benzoic acid have been examined in order to ascertain how the absorption is affected (1) by substitution in the nucleus; (2) when the nucleus and the acid radicle are separated by saturated or unsaturated aliphatic groups, as in phenylacetic, mandelic, cinnamic, and phenylpropiolic acids. The nuclear-substituted derivatives examined were the ortho-, meta-, and para-isomerides of toluic acid, chlorobenzoic acid, bromobenzoic acid, iodobenzoic acid, and nitrobenzoic acid.

In general, the spectra of the toluic acids and the halogen-substituted benzoic acids are of similar type, and it is noteworthy that iodine substitution does not destroy the bands as it does in benzene and toluene. At the same time, it is apparent that iodine produces a larger effect than the substitution of chlorine or bromine. This is shown by the decreased persistence and strength of the less refrangible band of the ortho and meta compounds, and the greater strength of the more refrangible band of the para-compound. The introduction of the nitro-group destroys the less refrangible band of benzoic acid and gives rise to a broad, weak band in the extreme ultra-violet. Similar effects are met with in the nitrocinnamic acids, but the influence of the ethenoid linking is apparent, for although the bands are weaker than in cinnamic acid itself, they have not been reduced to the same extent as in the nitrobenzoic acids.

The spectra of phenylacetic and mandelic acids show that the separation of the nucleus and the acid group leads to the reappear-

ance of residues of various benzene bands. This is not the case when an unsaturated group intervenes, as in cinnamic and phenylpropiolic acid, and it is suggested that the unsaturated valencies act as oscillatory centres, and thereby modify the vibrations of the nucleus. H. M. D.

Absorption and Dispersion of Light in Solutions of Dyes. BERN. J. VAN DER PLAATS (*Ann. Physik*, 1915, [iv], **47**, 429—462).—Various formulæ have been developed at different times to express the relation between absorption and dispersion. With the object of submitting these to the test of new experimental observations, the author has investigated the absorption and the dispersion of solutions of a number of dyes. The results obtained show that none of the formulæ afford dispersion curves which are in satisfactory agreement with the experimental curves. In general, the observed anomalous dispersion in the region of maximum absorption is considerably greater than that which corresponds with the theoretical relations.

In all cases it was found that absorption takes place in accordance with the requirements of Beer's law, provided that the solutions are non-fluorescent. The data for solutions of erythrosin show that Beer's law is applicable to 10, 3, and 1% solutions, but not to solutions of smaller concentration. Appreciable deviation was observed with a 0·5% solution, which is slightly fluorescent, and in the case of a 0·1% solution, which is strongly fluorescent, the divergence was found to be very large. H. M. D.

The Magnetic Spectrum of the Oxygen Canal Rays. T. RETSCHINSKY (*Ann. Physik*, 1915, [iv], **47**, 525—562).—A method described by Wien (A., 1910, ii, 475), which involves the use of a Rubens' linear thermopile, has been applied in the investigation of the spectrum which is produced when the canal rays from a discharge tube containing oxygen are made to pass through a magnetic field. The galvanometer readings which are obtained when the thermopile is moved across the beam of rays afford a means of determining the distribution of energy in the spectrum and the dependence of this distribution on the discharge potential; the current strength, the gas pressure, and the sign of the charge on the particles has been examined. The energy curves show the existence of several maxima. This result has been confirmed by the application of photographic methods.

From the observations, the conclusion is drawn that the canal rays contain three different kinds of particles, namely: (1) molecules carrying a single electric charge; (2) atoms with a single charge and a velocity about 1·4 times as great as that of the oxygen molecules; (3) singly charged atoms with a velocity equal to that of the molecules. The energy distribution in relation to these three types varies according to whether the particles are positively or negatively charged, but in both cases the number of slowly moving atoms is greater than that of the molecules or more rapidly moving atoms. The velocity of the particles is approxi-

mately proportional to the square root of the discharge potential, and increases when the gas pressure is reduced. These factors have, however, more influence on the slowly moving atoms than on those of higher speed. H. M. D.

The Influence of the Current Form on the Chemical Action of the Silent Electric Discharge. Ozone Formation. GEDEON LECHNER (*Zeitsch. Elektrochem.*, 1915, **21**, 309—324).—The current and *E.M.F.* curves for both alternating and interrupted direct current in the production of ozone have been obtained. Two series of experiments were carried out, the one with a glass ozoniser and the other with a metal ozoniser. The mean current strength is deduced from the form factor of the curves, and it is shown that Warburg and Leithäuser's rule, "that the yield of ozone is proportional to the mean current strength," is true. The yield of ozone when the ozoniser is suitably electrified is almost independent of the curve form. Generally, the experimental results show that the flatter current and *E.M.F.* curves are more efficient, since the yield per watt-hour and the efficiency factor are larger under these conditions. This point is of importance in the construction of ozone generators for commercial purposes. When an alternating current is used with a metal ozoniser, it is shown that a partial conversion into direct current occurs. J. F. S.

Theory of Liquid [Surface] Potential Differences. I. K. H. A. MELANDER (*Zeitsch. physikal. Chem.*, 1915, **90**, 59—69).—A theoretical paper in which the calculation of liquid contact potential differences is discussed. It is shown that the undissociated molecules must be considered in making these calculations. Two cases, (1) where there is only one electrolyte concerned, and (2) where there are two electrolytes with a common ion concerned, are treated mathematically. It is shown in the second case that

$$\pi = -R/\epsilon \int_{c\pi}^{cr} \{(\alpha' - \alpha v/K'.K'')c^2 - k(u' - u'')\}/\{(\alpha' + \alpha v/K'K'')c^2 - 2(u' - u'') + k(u' - u'')\} \, . \, dc/c,$$

where π is the potential difference, ϵ the charge per equivalent, c the concentration of the anion, α' and α the degree of dissociation, K' and K'' the dissociation constants, u' and u'' the velocities of the cations, v the velocity of the anion, and k a constant.

J. F. S.

The Hypochlorite-Carbon Cell as a New Type of Galvanic Element. A. THIEL (*Zeitsch. Elektrochem.*, 1915, **21**, 325—329).—A theoretical paper in which the hypochlorite–carbon cell of Hofmann and Ritter (A., 1914, ii, 612) is considered. It is shown that a true galvanic cell is constituted by the hypochlorite–carbon cell which supplies current indirectly from the free energy of oxidation of carbon to carbon dioxide. The action is not direct between the carbon and the hypochlorite, but is due to the oxida-

tion potential of the hypochlorite, which causes a liberation of oxygen on the carbon; the oxygen then, before it combines to form molecules, is used up in oxidising the carbon. The rôle of the carbon is therefore that of a depolariser, which acts in a purely chemical manner, and not like most depolarisers in an electrochemical manner. The new element, therefore, represents a new type of galvanic element, which acts both chemically and electrochemically. It is a half electrochemical oxidation and reduction element. The existence of this cell proves that purely chemical processes, when coupled with electrochemical processes, can be used for the production of electricity. It is also shown to be probable that in this cell the *E.M.F.* is conditioned by the velocity of depolarisation, and not by an equilibrium between the carbon and oxygen. J. F. S.

Electromotive Force of Magnesium Amalgams. Livio Cambi (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 932—936. Compare this vol., ii, 453).—The author has measured the differences of potential between magnesium and its amalgams and solutions of magnesium chloride and iodide in methyl-alcoholic and in pyridine solution. The values of ϵ_H for $MgHg_2$ and Mg in methyl alcohol at $-80°$ are $-1{\cdot}634$ and $-1{\cdot}818$ volt respectively. The influence of the solvent on the potentials of metals is exerted also with amalgams. In pyridine, both magnesium and its amalgams exhibit phenomena of passivity, which are shown either not at all or but slightly, when methyl alcohol is used as solvent. The potential of magnesium is appreciably lower than that of calcium, but that of the magnesium amalgam, $MgHg_2$, is slightly higher than that of the calcium amalgam, $CaHg_4$ (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 599). T. H. P.

Strip Electrodes. Heinrich Göckel (*Chem. Zeit.*, 1915, **39**, 484).—Electrolytic apparatus, in which platinum foil electrodes are fused lengthwise through the glass, has been made, and is of value in operations where efficient cooling is essential, the external strip of the electrode being immersed in a cooling bath, the heat from the adjacent internal portion being thus conducted rapidly away. These electrodes are employed in the apparatus described by Hauser and Herzfeld for the estimation of methane in the air (this vol., ii, 587). G. F. M.

Magnetic Rotation of the Plane of Polarisation in Titanium Tetrachloride. L. H. Siertsema (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 101—106).—In order to ascertain whether the dispersion formulæ derived on the basis of the electron theory are in agreement with the observed magnetic dispersion, measurements have been made of the magnetic rotation of titanium chloride for light of wave-length ranging from λ 4358 to λ 6452. The special interest which attaches to this substance is that it is the only liquid diamagnetic substance which shows negative magnetic rotation. The data obtained are to be discussed in a later paper.

H. M. D.

An Extension of Trouton's Rule. SVANTE ARRHENIUS (*Medd. K. vetens. Nobel-institut.*, 1915, **3**, No. 6, 1—9).—The author in his text-book, "Lehrbuch der kosmischen Physik," pp. 158—163, has made the statement "that chemical processes give out more heat the higher the temperature at which they take place, and that in all probability the heat evolution will be proportional to the absolute temperature at which the process takes place." This statement is now confirmed by calculation of the ratio Q/T for a number of reactions which have been studied in recent years. It is shown that for reactions where n molecules become $n+1$ molecules, the ratio $Q/T=36{\cdot}4$ (mean) in cases of reactions of n molecules becoming $n+2$ molecules, about double this value is obtained for Q/T, and in a few cases where n molecules become n molecules, very low values are obtained for the ratio; thus, for $2HCl \rightleftarrows H_2+Cl$, $Q/T=0{\cdot}88$. The theoretical bearing of the relationship is discussed. J. F. S.

Properties of Cold-worked Metals. I. The Density of Metallic Filings. THOMAS MARTIN LOWRY and REGINALD GEORGE PARKER (T., 1915, **107**, 1005—1018).—It is probable that metallic filings afford an extreme instance of the effect of hardening which is produced by cold-working, and experiments have been made to determine the changes in density which are brought about, first by filing and then by annealing the filings at different temperatures. The changes in density due to filing were measured pyknometrically, and those produced by annealing were investigated by means of dilatometers. The pyknometric data are in agreement with the general rule that the density of a metal is always diminished by working. It would seem that deformation and slipping give rise to a change of state which is accompanied by an increase in the volume, notwithstanding the fact that the metal may be under strong compression during the process.

The annealing experiments afford confirmation of the rule that the complete annealing of metallic filings is accompanied by a contraction of volume. This contraction is ascribed to the recrystallisation of amorphous metal produced by working (compare Beilby, A., 1904, ii, 647).

From observations on partial annealing at progressively increasing temperatures (100°, 180°, and 240°), it has been found that the process apparently involves three distinct changes, that is to say, two changes in addition to the final contraction due to recrystallisation. This contraction is preceded by an expansion, which appears to be universal and independent of the nature of the metal. In certain cases, namely, gold, silver and copper, cobalt, nickel and antimony, the expansion is preceded in its turn by a preliminary contraction. The preliminary contraction and the intermediate expansion of gold can be observed to take place consecutively when gold filings are annealed at 100°, but in general these component changes can only be distinguished when the temperature is altered.

It is pointed out that the preliminary contraction and inter-

mediate expansion may find an explanation in the occurrence of allotropy and on the basis of Heyn's strain theory (*J. Inst. Metals*, 1911, **12**, 3). H. M. D.

Experiments on Supersaturated Solutions. MARIAN JONES and JAMES RIDDICK PARTINGTON (T., 1915, **107**, 1019—1025).—The influence of the size of the particles on the solubility of gypsum has been investigated by measuring the electrical conductivity solutions in equilibrium with (*a*) large crystals; (*b*) finely powdered substance which had been passed through a silk sieve. Measurements at 19·60°, 40·0°, and 59·95° gave the following values for the specific conductivity, the numbers in brackets having reference to the finely divided gypsum: 0·001980 (0·002068); 0·002892 (0·003153); 0·003624 (0·003765).

By application of Gibbs' theory in the form of the equation $RT/M \cdot \log_e s_r/s_\infty = 2\sigma/\rho r$, where R is the gas constant, T the absolute temperature, M the molecular weight, s_r the concentration of the solution in equilibrium with spherical particles of radius r, s_∞ that of the normally saturated solution, σ the surface energy per unit area, and ρ the density of the solid substance, the authors have calculated the solubility of gypsum for values of r between $r=0{\cdot}5\ \mu$ and $r=50\ \mu$, and for temperatures ranging from 0° to 90°. The influence of the size of the particles has practically disappeared when the radius exceeds $50\ \mu$. A comparison of the experimental numbers with curves which represent the results of the above calculations shows that the powdered gypsum used in the experiments consisted of particles of radius approximately equal to 10^{-4} cm.

Experiments are also described which show that calcium acetate and butyrate yield supersaturated solutions of the second type (compare this vol., ii, 45). H. M. D.

Molecular Condition of Mixed Liquids. II. Applications of Traube's Atomic Volume Method to Binary Mixtures. WILLIAM RINGROSE GELSTON ATKINS and KATHLEEN SHIPSEY (T., 1915, **107**, 1117—1121. Compare P., 1910, **26**, 337; T., 1913, **103**, 1461).—The molecular volumes of forty-six equimolecular binary mixtures have been calculated by means of the Traube formula $V_{m+m'} = \Sigma$ atomic volumes + 2 co-volumes. It is shown that when the Traube method indicates the presence of a compound, this result is generally in accordance with evidence obtained from other methods. In many cases, however, results, which indicate the presence of compounds, are obtained which are due to the average of the association factors of the two liquids having a value in the neighbourhood of two. J. F. S.

A Simple Viscosimeter for the Determination of the Viscosity of Volatile Liquids and Mixtures of Volatile Liquids. O. FAUST (*Zeitsch. Elektrochem.*, 1915, **21**, 324).—The author describes a modification of the Ostwald viscosimeter for use in determining the viscosity of liquids at temperatures near their boiling points. The

two limbs of the Ostwald instrument are connected by a glass U-tube, and a side-tube with tap is attached to each limb of the viscosimeter. A stoppered side-tube is attached to the wider limb for filling, and a further stopcock is placed in the connecting U-tube. The whole of the liquid is thus enclosed, and so shielded from changes in concentration, in the case of mixtures, by evaporation. The side-tubes serve for blowing or drawing the liquid to the required position for making a measurement. J. F. S.

The Temperature-coefficients of the Free Molecular Surface Energy of Liquids at Temperatures from −80° to 1650°. IX. The Surface Energy of Homologous Aliphatic Amines. F. M. JAEGER and JUL. KAHN (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 75—91. Compare A., 1914, ii, 806, 840).—By the method described in the previous papers, the authors have made measurements of the surface tension of a number of amines at different temperatures, and from these data, in combination with corresponding measurements of the density, they have deduced the value of the temperature-coefficient of the molecular surface energy. The nature of the results is shown in the following summary, which gives the temperature-coefficients of the molecular surface energy, and also the equation for the change of density with the temperature. Where the temperature-coefficient of the surface energy varies with the temperature, the limiting values are given, the first value relating to the lowest range of temperature: methylamine, 1·20 − 1·83, $D = 0·6831 - 0·00109t$; dimethylamine, 1·10, $D\ 0·6804 - 0·0009886t$; trimethylamine, 1·89 − 1·33, $D\ 0·6709 - 0·001048t$; ethylamine, 1·25, $D\ 0·7085 - 0·001032t$; diethylamine, 1·69, $D\ 0·7315 - 0·00107t - 0·0^{6}4t^{2}$; triethylamine, 2·56 − 1·71, $D\ 0·7495 - 0·00095t - 0·0^{6}4t^{2}$; *n*-propylamine, 1·54, $D\ 0·741 - 0·001075t$; dipropylamine, 2·38 − 1·69, $D\ 0·7565 - 0·00095t + 0·0^{6}4t^{2}$; tripropylamine, 2·41; $D\ 0·773 - 0·0008t$; *iso*propylamine, 1·76, $D\ 0·691 - 0·001t$; allylamine, 1·40, $D\ 0·785 - 0·0011t$; *n*-butylamine, 1·82 − 1·02, $D\ 0·764 - 0·001t$; *iso*butylamine, 1·44, $D\ 0·7505 - 0·00104t$; di*iso*butylamine, 2·40, $D\ 0·763 - 0·00086t$; tri*iso*butylamine, 1·44 − 2·61, $D\ 0·782 - 0·0007t - 0·0^{6}8t^{2}$; *tert.*-butylamine, 1·85 − 1·25, $D\ 0·716 - 0·001048t - 0·0^{5}1t^{2}$; *n*-amylamine, 1·68, $D\ 0·770 - 0·00098t + 0·0^{6}8t^{2}$; *iso*amylamine, 1·88, $D\ 0·771 - 0·00098t + 0·0^{6}8t^{2}$; di*iso*amylamine, 2·37, $D\ 0·784 - 0·00084t + 0·0^{6}8t^{2}$; *tert.*-amylamine, 2·54 − 3·9, $D\ 0·756 - 0·00102t + 0·0^{6}8t^{2}$; *n*-hexylamine, 1·03 − 2·50, $D\ 0·7855 - 0·00088t - 0·0^{6}8t^{2}$; *iso*hexylamine, 1·51, $D\ 0·780 - 0·00086t - 0·0^{6}8t^{2}$; *n*-heptylamine, 1·52 − 1·96, $D\ 0·7875 - 0·0009t$.

In general, the observations show that the substitution of hydrogen by alkyl radicles is accompanied by an increase in the surface energy when the comparison is made at a fixed temperature. In the case of isomeric amines, those with unbranched hydrocarbon chains have at a fixed temperature a greater surface energy than those with branched chains. On comparing the primary, secondary, and tertiary amines, it is found that the temperature-coefficients of the surface energy are, generally speak-

ing, larger for the secondary than for the primary and tertiary amines. H. M. D.

Structure of the Capillary Layer. G. Bakker (*Zeitsch. physikal. Chem*, 1915, **90**, 89—120. Compare A., 1914, ii, 179).—A theoretical paper in which it is shown that the irregularity in the movement and position of the molecules, in the liquid vapour and transitional layer of substances, makes it possible and necessary to replace the substance of the system by a medium (Agens). The force of attraction between the elements of this medium is represented by the potential function $-f.e^{r/\lambda}/r$, in which λ represents a small length, which is of the order of magnitude of the mean distance between the liquid molecules. If ϵ, ϵ_1, and ϵ_2 represent the energy of the capillary layer, the liquid, and the vapour, respectively, per unit mass, then $\epsilon_1+\epsilon_2/2-\epsilon=\Delta\epsilon$, and if M is the molecular weight, N the Avogadro number, and n the number of molecular layers in the capillary layer, then, if the value of M does not change on passing from liquid to vapour,

$$\frac{\Delta\epsilon}{r_i}\frac{1}{2}\frac{\phi_1-\phi,}{\phi_1+\phi_2}-\frac{1}{n}\frac{\sqrt[3]{\phi_1}+\sqrt[3]{\phi_2}}{\phi_1+\phi_2}\sqrt[3]{\frac{N}{M}}\frac{H-T.dH/dT}{r_i}$$

in which ϕ_1 and ϕ_2 are the densities of the liquid and vapour respectively, H is the surface tension, and r_i the inner heat of vaporisation. This formula has been tested by known data for benzene and ether at a series of temperatures. At 80°, for benzene the value of r is found to be $40{\cdot}4\times10^8$ ergs., whereas at 80·2° Brown found $r=39{\cdot}8\times10^8$ ergs. If under the thickness of the capillary layer is understood a length, below which the transition layer between liquid and vapour cannot be taken without neglecting too much of the value of the energy of the capillary layer and of the surface tension, then it is found that for temperatures in the region of the melting point, the number of molecular layers (n) in the capillary layer lies between 3 and 4. At temperatures between $0{\cdot}7T_k$ and $0{\cdot}8T_k$, the value of n is 5—6. Only in the region of the critical temperature has n larger values: for $T=0{\cdot}97T_k$ – $0{\cdot}99T_k$, $n=12$—15, and at temperatures still closer to the critical temperature the value of n increases very much. Thus, in the case of ether at $T=0{\cdot}997T_k$, $n=27$—92; for carbon dioxide at $T=0{\cdot}999T_k$, n is between 300 and 2000. This large value of n has nothing to do with the increase in the value of the radius of the sphere of influence; this is chiefly a result of the fact that the gradient of the density in the neighbourhood of the critical temperature is very small. The radius of the sphere of influence is approximately six to seven times the mean distance between the molecules of the liquid. J. F. S.

Gas Solubility in Aqueous Solutions of Glycerol and Chloral Hydrate. A. von Hammel (*Zeitsch. physikal. Chem.*, 1915, **90**, 121—125).—The solubility and absorption coefficient of nitrogen and carbon dioxide have been determined in aqueous solutions of

glycerol and chloral hydrate of various concentrations at 15°. The results confirm those of Müller (A., 1913, ii, 30). It is shown that there is no minimum of solubility as indicated by Müller, but in all other respects the results and conclusions of Müller are confirmed. J. F. S.

An Hypothesis on the Condition of Dissolved Electrolytes. I. H. C. S. Snethlage (*Zeitsch. physikal. Chem.*, 1915, **90**, 1—46).—A theoretical paper which, from the author's experiments and those of other investigators on velocity of esterification, molecular weight determination, electrical conductivity, and absorption spectra, it is shown that the Arrhenius hypothesis is not applicable to solutions of electrolytes in ethyl alcohol and methyl alcohol. In these solvents, electrolytes are to be arranged into two groups. (1) The strong electrolytes, such as hydrochloric acid and salts; the whole of the properties of these solutions are proportional to the total concentration of the electrolyte or a simple function of it. The function Δ_v/Δ_∞ in this case has no meaning in the calculation of the typical properties of these solutions. (2) The majority of organic acids and bases; solutions of these substances do not show the same proportionality as the electrolytes of group 1. Solutions of these electrolytes exhibit an increased activity with decreasing concentration. This change in the case of electrical conductivity follows the Ostwald dilution law, and in the case of catalytic activity follows the formula

$$k_R = \{\Delta_v/\Delta_\infty \,.\, k_H + (1 - \Delta_v/\Delta_\infty)\,.\, k_M\}\,1/v,$$

in which k_R represents the velocity constant due to the whole acid, k_M that due to the molecules, and k_H that due to the hydrogen ions. The behaviour of electrolytes of the second group is explained by the assumption that the properties of these solutions do not depend on the presence of free ions, which change their concentration relatively to the concentration of the electrolyte, but on a definite property of the dissolved molecules. These molecules exhibit a polarity, and are therefore active. In the first group, if the concentration is not too great, the whole of the molecules are in this condition, and the change which occurs at high concentrations cannot be explained by a change in the degree of dissociation. In the second group an equilibrium, which depends on the concentration, exists between the active and inactive molecules, and the relative concentration of the two forms is given approximately by Δ_v/Δ_∞. The active molecules, with respect to their electrolytic properties, are practically identical with the molecules of the first group. The dissociation constant gives the equilibrium between the active and inactive molecules, and is dependent, in a high degree, on the nature of the solvent. The change of molecular conductivity with concentration in the case of electrolytes of the first group is the result of a mutual inter- or intra-molecular action, and in consequence the difference between Δ_∞ and the molecular conductivity at any dilution is proportional to the mean distance between the molecules. The value of Δ_∞ is reached when the concentration is so small that the disturbing influences vanish,

and this value gives a measure of the electrolytic and catalytic activity. In the second group, the change in equivalent conductivity is due to the transition of inactive molecules into active molecules. The concentration of the active molecules here is so small that the mutual influences do not appear, and the value Λ_∞ is reached when the concentration is so small that the whole of the molecules have become active. The activity of the molecules is explained by the introduction of an electron into the molecule, whereby the molecule becomes bipolar, but a division into free ions, in the sense of the dissociation hypothesis, does not take place. The forces existing between these poles are determinative of the properties of electrolytes, and probably of the affinity. The differences observed between equally concentrated dilute solutions of electrolytes containing a common ion are to be explained by this view. A further property is also determinative of the catalytic and electrolytic activity of the molecule, namely, the mutual action between the solvent and the dissolved molecule—solvation. Solvation depends, finally, on the activity of the molecule. A large value of Λ_∞ goes hand in hand with strong catalytic activity and strong solvation, and vice versa. This is probably true for the active molecules of both groups. In consequence of this explanation, other electrolytes (salts) can catalyse reactions in the same way as the acids, and since in these cases there is no hydrogen ion, it follows that in acid catalysis the real catalyst is the active molecule of the acid. The solvent plays a further part in the change from inactive to active molecules of electrolytes of the second group. If the active molecule is regarded as "solvated," then the change can be represented: inactive molecule + solvent $\longrightarrow$ solvated active molecule. The question of the meaning of the term ion in this connexion is discussed. J. F. S.

Dissociation of Electrolytes as a Function of the Neutral Molecule. Bohdan de Szyszkowski (*Medd. K. vetens. Nobel-institut.*, 1915, **3**, No. 2, 1—50).—A theoretical paper in which a general discussion of the various formulæ which have been put forward to represent the dissociation of electrolytes is entered into. The author advances reasons for regarding the formula $D=K+k(c^{\frac{1}{3}})^m$ as being the most satisfactory. In this formula, D is the dissociation function, K the true dissociation constant, c the concentration, k the dissociation coefficient, and m an arbitrary coefficient. This formula, when written in the form $\alpha^2c/(1-\alpha)-K=k(c^{\frac{1}{3}})^m$, expresses the fact that the dissociation function $\alpha^2c/(1-\alpha)-K$ increases proportionately with the linear concentration $(c^{\frac{1}{3}})$ when $m=1$, or to some power of the linear concentration when $m\lesssim 1$; this may be taken to indicate that the dissociation function is inversely proportional to the mean free path (l) of the undissociated molecules. So that at high dilutions, when $c_\infty=0$ or $l=\infty$, the equation becomes $\alpha^2c/(1-\alpha)=K$, and the dissociation follows the law of mass action; but as soon as the concentration becomes sufficiently great, each molecule begins to exert a mutual influence on the others and increases the dissociation. The above formula is

tested on the best obtainable conductivity values of thirty-four electrolytes in aqueous solutions. The formula is held to be true for non-aqueous solutions from analogies which exist between it and the formula of Kraus and Bray (A., 1913, ii, 914). The examination of the formula shows that in all probability Walker's hypothesis that the deviations of strong electrolytes are due to the un-ionised molecules, and not to the ions, is true, since this expression is found to be applicable, without exception, to all salts and acids up to a concentration of $0{\cdot}5N$. The power of the neutral molecule to increase the ionisation (a) has been calculated for a large number of electrolytes, and the results tabulated. These values vary between 6 and zero, the smallest being 0·00025. The existence of a true dissociation constant K for all electrolytes is proved; for salts this has approximately the value 0·01.

J. F. S.

Solubility of Electrolytes in Salt Solutions. Bohdan de Szyszkowski (*Medd. K. vetens. Nobel-institut*, 1913, **3**, No. 5, 1—26). —The solubility of salicylic acid, 3 : 5-dinitrobenzoic acid, *o*-nitrobenzoic acid, and *m*-amino-benzoic acid, have been determined in water and in water containing known quantities of sodium chloride or potassium chloride, and in some cases in the presence of benzene. As a result of the determinations, and also theoretically, it is shown that the increase in solubility of the weak electrolytes used, which in many cases rises to a maximum at a given salt concentration, is a natural consequence of double decomposition, as well as of an increase of the affinity constant caused by the presence of the salt. It is held that the non-dissociated part of the electrolyte is decreased in solubility by the dissolved salt in the same way as the solubility of a non-electrolyte is decreased by the presence of salts, the depression of solubility of the non-dissociated part being given by the equation $c_s(1-x/c_s)(1-\alpha_s)/c(1-\alpha)=1-f$, where c_s is the solubility of the electrolyte in salt solution, x the concentration of the amount of the electrolyte which has undergone double decomposition, α_s the degree of dissociation of the electrolyte in salt solution, c the solubility of the electrolyte in water, α the degree of dissociation of the electrolyte in water, and f a function of the salt concentration.

J. F. S.

Hydrated and Complex Molecules in Non-associated Solvents. I. Bohdan de Szyszkowski (*Medd. K. vetens. Nobel-institut.*, 1915, **3**, No. 4, 1—26).—The author has determined the solubility of benzoic acid, salicylic acid, 3 : 5-dinitrobenzoic acid, and *o*-nitrobenzoic acid in dry benzene, dry chloroform, and in these solvents in the presence of an excess of water at 25°. The solubility is much greater in the presence of water, and this is shown to be due to the formation of hydrates in the organic solvent. A second series of determinations of the solubility of the following binary mixtures of acids in benzene, salicylic and benzoic, salicylic and *o*-nitrobenzoic, and salicylic and dinitrobenzoic, shows that these acids form complexes in benzene solution. The solubility of the same

binary mixtures is determined in benzene in the presence of excess of water, and it is shown that, to a limited extent, ternary molecules of the two acids and water exist in benzene solution. Finally, solubility determinations of salicylic acid, benzoic acid, and *o*-nitrobenzoic acid are made in benzene in the presence of an excess of water. It is shown in this case that ternary molecules of the three acids exist in the benzene, and it is not unlikely that these ternary molecules are hydrated to some extent. J. F. S.

Hydrated and Complex Molecules in Non-associated Solvents. II. BOHDAN DE SZYSZKOWSKI (*Medd. K. vetens. Nobel-institut.*, 1915, **3**, No. 9, 1—20. Compare preceding abstract).—A continuation of the work described in a previous paper (*loc. cit.*). In the present paper further proof is brought to show that the increase in solubility in moist benzene is due to the formation of hydrates and complexes. Four systems of three acids and water in benzene, and one system of four acids in water and benzene, are considered. The systems of acids investigated are: (1) salicylic acid, *o*-nitrobenzoic acid, and 3 : 5-dinitrobenzoic acid, and (2) *m*-nitrobenzoic acid, *o*-nitrobenzoic acid, 3 : 5-dinitrobenzoic acid, and salicylic acid. The method of investigation is exactly the same as described in the previous paper. The complete investigation of a system of three acids involves the determination of: (i) the solubility of each acid in dry benzene and in moist benzene; (ii) the association constant of the simple molecules of each acid in benzene; (iii) the solubility of the three pairs of acids in dry and moist benzene; and (iv) the solubility of the three acids together in dry and moist benzene. The results in all cases point to the formation of hydrated complexes in moist benzene solutions and to anhydrous complexes in dry benzene solutions. J. F. S.

Influence of Temperature on the Association and Hydration of Acids in Benzene. BOHDAN DE SZYSZKOWSKI (*Medd. K. vetens. Nobel-institut.*, 1915, **3**, No. 10, 1—11. Compare preceding abstracts). —The distribution and solubility of *m*-nitrobenzoic acid, *o*-nitrobenzoic acid, salicylic acid, 3 : 5-dinitrobenzoic acid, and benzoic acid have been studied at 25° and 40° with the solvents water and benzene. It is shown that the nitrobenzoic acids associate to form quadruple molecules; this association is greater for *o*-nitrobenzoic acid than for *m*-nitrobenzoic acid. The dissociation constants of the double molecules of these acids do not vary much with change of temperature at the concentrations concerned. In the case of the nitrobenzoic acids and salicylic acid, the degree of hydration in moist benzene solution increases with temperature. It is pointed out that the conclusions arrived at in the present and preceding papers for water and benzene solution, that is, for an associated and a non-associated solvent, cannot be applied to other pairs of solvents unless one of the pair is associated and the other non-associated; also no conclusions can be drawn as to the condition of the dissolved substance in the water. In this connexion, the views of Hantzsch (A., 1900, ii, 69; 1901, ii, 8) are criticised.

J. F. S.

A Relation Concerning the Distribution of an Electrolyte Between Water and some Second Solvent, and its Dissociation Constant in Aqueous Solution. HENRY JERMAIN MAUDE CREIGHTON (*J. Franklin Institute*, 1915, **180**, 63—74).—The author holds that the non-agreement of the Ostwald dilution law for many electrolytes is due to inaccurate determination of the degree of dissociation. He devises a method of obtaining this value from distribution values, and evolves an expression which, taking account of association, allows of the calculation of the degree of dissociation. This expression has the form

$$z = c' - c\sqrt{(b'(1-x') + \sqrt[n]{b'x'})/b(1-x) + \sqrt[n]{bx}}\Big/(b'(1-x') + \sqrt[n]{b'x'})/$$
$$(b'(1-x) + \sqrt[n]{bx}) - \sqrt{(b'(1-x') + \sqrt[n]{b'x'})/(b(1-x) + \sqrt[n]{b'x}),}$$

in which c is the total concentration of the electrolyte in the aqueous phase, b the total concentration of the electrolyte in the second phase, x the degree of association of the electrolyte in the second phase, n the complexity of the molecules in the second phase, and $z = K_1 b(1-x)$, where K_1 is the distribution ratio of the normal molecules between the two phases, the values c', b', x' have the same meanings for a different initial concentration. This equation is tested by means of distribution experiments on benzoic acid between water and benzene at 6°, and association determinations of benzoic acid in benzene. The formula is found to hold, and the value at 6° for the dissociation constant is found to be $7{\cdot}21 \times 10^{-5}$, which is slightly higher than that obtained from conductivity determinations. J. F. S.

[Experimental Confirmation of the New Theory of Allotropy.] A. SMITS (*Zeitsch. physikal. Chem.*, 1915, **90**, 126).—Polemical, an answer to Kruyt (this vol., ii, 322; compare A., 1910, ii, 195, 400; 1913, ii, 393, 933). J. F. S.

Allotropy and Metastability of Metals. ALFRED HOLT (*J. Soc. Chem. Ind.*, 1915, **34**, 693—697).—A summary and review of present knowledge of the allotropic modifications of metals, based largely on the work of Cohen and Smits. The authors object is to show that many of the phenomena connected with the various modifications assumed by metals may be explained on the basis of a theory of monotropic, enantiotropic, or dynamic allotropy. G. F. M.

Invariant, Univariant, and Bivariant Equilibria. I. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 116—126).—A theoretical paper, in which it is shown that a knowledge of the composition of the phases in an invariant system and of the changes in volume and entropy which are characteristic of the various transformations, affords a means of determining the equilibrium curves in the pressure-temperature diagram. H. M. D.

Hydrogenation Equilibria. M. PADOA and B. FORESTI (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 946—948).—With the aid of the critical pressures and latent heats of evaporation determined by

Grassi (1914, ii, 765), the authors have calculated the following chemical constants: (1) from Nernst's two formulæ (*loc. cit.*); (2) from Trouton's rule; and (3) from Trouton's corrected formula, $C = 1{\cdot}331 \log T - 0{\cdot}00098T$, where T is the absolute boiling point:

	(1.)	(2.)	(3.)
*iso*Propyl alcohol	4·94	3·71	3·044
Acetone	3·74	3·08	3·025
Diethylcarbinol	4·51	3·39	3·063
Diethyl ketone	4·54	2·92	3·056
Benzene	4·37	2·9	3·043
*cyclo*Hexane	4·30	2·85	3·043

These results are used for the calculation of the equilibrium constants of the two equilibria previously studied (this vol., ii, 325). The values thus obtained by means of Nernst's formulæ differ markedly from the actual experimental values, and errors in the latter do not appear to be the cause of such divergence. The equilibrium constants deduced on the basis of Trouton's rule, or on that of the absolute boiling-point equation, are in far better agreement with the experimental data.

The conclusion is drawn that the calculation of chemical constants by means of the formulæ as yet proposed does not lead to accurate results, especially in the case of processes accompanied by small thermal changes. T. H. P.

Influence of Neutral Salts on Chemical Equilibrium. G. Poma and G. Albonico (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 979—985. Compare this vol., ii, 431).—The influence of other chlorides on the equilibrium,

$$CH_3{\cdot}CO_2H + Me{\cdot}OH \rightleftarrows H_2O + CH_3{\cdot}CO_2Me,$$

has been studied, the experimental conditions being those used previously.

Calcium and magnesium chlorides accelerate the velocities of both the esterification and the hydrolysis, the former change being influenced to a greater extent than the latter, so that the equilibrium constant, $K = k_2 : k_1$, is diminished. The displacement of the equilibrium is least for lithium chloride, greater for calcium chloride, and greatest for magnesium chloride.

The presence of increasing proportions of hydrochloric acid produces variations in the value of the equilibrium constant, K, of the same order of magnitude as those obtained with the neutral salts, but the increases of k_1 and k_2 are in this case more rapid. Each of these two velocity constants increases more rapidly than the concentration of the hydrochloric acid; thus, increase of the latter from $0{\cdot}2N$ to $1{\cdot}0N$ causes k_1 to change from 0·00240 to 0·01537, and k_2 from 0·00041 to 0·00247. These results support the view that the catalytic activity of undissociated molecules of strong acids is greater than that of free hydrogen ions.

Measurements have also been made with ethyl in place of methyl alcohol. T. H. P.

The Partition Law. G. von Georgievics (*Zeitsch. physikal. Chem.*, 1915, **90**, 47—58).—The partition law is discussed, and it is shown

that the partition of a substance between water and a hydrocarbon is probably due to the same process as occurs in the absorption of substances from aqueous solution by solid substances. It is shown from distribution experiments of monochloroacetic acid, dichloroacetic acid, benzoic acid, salicylic acid, and trichloroacetic acid between water and benzene that the characteristic x value of sorption experiments has the same meaning as the x value of distribution of substances between water and benzene. Consequently, the laws of partition cannot be regarded as true, and the solution of a substance in a liquid may not be regarded in all cases as a simple process. A further series of experiments on the partition of pyridine, piperidine, and hydrazine between water and benzene confirm these conclusions, and show that the affinity of these bases for water is smaller than that of the acids mentioned above. J. F. S.

Distribution of Dinitrobenzoic Acid. Bohdan de Szyszkowski (*Medd. K. vetens. Nobel-institut.*, 1915, **3**, No. 3, 1—7).—The partition of 3 : 5-dinitrobenzoic acid has been determined between water and benzene and between water and chloroform, using the same method as previously described (A., 1914, ii, 114). Making use of Kendall's value of k for dinitrobenzoic acid (T., 1912, **101**, 1292), the disintegration constants of bimolecular dinitrobenzoic acid in the three solvents are calculated, the values obtained being: water, $1{\cdot}60 \times 10^{-3}$; chloroform, $3{\cdot}60 \times 10^{-3}$; and benzene, $4{\cdot}80 \times 10^{-3}$. This shows that the acid is very highly associated in water, and less so in the other solvents, a fact which is in direct contradiction to the Thompson-Nernst dielectric constant rule, according to which the association should be greater the smaller the dielectric constant. J. F. S.

Theory of Reactions Occurring in Stages, Particularly of the Formation and Saponification of Esters of Dicarboxylic Acids. Rud. Wegscheider (*Monatsh.*, 1915, **36**, 471—495).—A theoretical paper, in which the development of the theory of reactions which occur in stages is traced, with special reference to the formation and saponification of esters of dicarboxylic acids. Formulæ are given for reactions occurring in two stages in the presence of a large excess of the reagent, both with and without the intermediate formation of isomeric products, in the general case and also in that in which the reaction appears to be unimolecular.

The formation and saponification of esters of dicarboxylic acids without doubt takes place in steps, since acid esters are isolated from such reactions. In this case, however, it remains to be proved that the changes take place entirely in this way.

Proportionality between the number of active groups in the molecule and the velocity constants of the different actions is frequently not observed even in those cases in which deviations from proportionality cannot be explained by an electrostatic action of the ions.

The course has been investigated which the velocity constants of a bimolecular reaction taking place in two stages must follow if calculated as taking place in one stage. This is different according as the initial concentrations of the transformed substance are expressed in equivalents or mols. From this, rules are deduced for obtaining approximate values for the constants of reactions occurring in stages by calculating on the basis of a one-stage change. H. W.

The Velocity of Reaction Between Chlorine and Hydrogen at High Temperatures. KARL H. A. MELANDER (*Arkiv. Kem. Min. Geol.*, 1914, **5**, No. 12, 1—22).—The velocity of reaction between chlorine and hydrogen at 205°, 239°, and 255° has been determined. The gas mixtures were contained in borosilicate vessels connected with a spiral manometer, so that the pressures during filling, and hence the partial pressures, could be measured, and also connected with an evacuated vessel so that the gases could be drawn off at any time for analysis. The gases were well mixed by means of a porcelain ball, which could be rolled about in the borosilicate vessels.

The reaction is bimolecular, taking place according to the equation $-d[Cl_2]/dt = K[Cl_2][H_2]$. The temperature quotient for 10° is 2·01, and preliminary heating of the chlorine has no effect on the velocity. The presence of sulphuric acid or of sulphur dioxide has a very marked accelerating action, which can be explained by assuming the intermediate formation of sulphuryl chloride; the order of the reaction is not thereby changed, since it is readily shown that the concentration of the sulphuryl chloride is directly proportional to that of the chlorine. T. S. P.

Kinetics of the Bromate–Nitrite Reaction. ALBIN KURTENACKER (*Monatsh.*, 1915, **36**, 451—456).—In a previous communication (A., 1914, ii, 552), the author has shown that the velocity of the reaction between nitrite and bromate is independent of the concentration of the former when it is present in relative excess, and has put forward the theory that the oxidation does not affect the nitrite itself, but the nitric oxide obtained by its decomposition. Experimental proof is now afforded by an investigation of the influence of pressure and temperature on the velocity of the reaction.

Diminution of pressure may be expected to decrease the reaction velocity, owing to decrease in concentration of nitric oxide. This is shown to be actually the case, but the extent of the decrease is scarcely so great as would be expected. It is suggested that a second factor is involved, possibly an increased instability of nitrous acid, due to the lower pressure.

The effect of temperature on the velocity of the reaction is shown to be that which would be expected if oxidation affects the nitric oxide. H. W.

Thermodynamics of the Sulphuryl Chloride Equilibrium $SO_2 + Cl_2 \rightleftarrows SO_2Cl_2$. IV. The Velocity of the Reactions which bring about Equilibrium. MAX TRAUTZ (*Zeitsch. Elektrochem.*, 1915, **21**, 329—342. Compare A., 1908, ii, 569).—Using the same method as previously adopted, the velocity of the formation and decomposition of sulphuryl chloride has been determined. It is shown that neither reaction occurs between 18° and 190° in the dark, but on the addition of a little animal charcoal both reactions occur as adsorption reactions, which are little influenced by diffusion. The order of the reaction is in both cases approximately normal, but more nearly normal for the decomposition than for the formation. In the latter case, the velocity constant decreases rapidly toward the end of the reaction. The temperature-coefficient of the formation is 1·0, that of the decomposition 1·5, but both values must be regarded as too small, on account of the opposing action of the adsorption. The kinetic integration constants calculated from these values are, for the formation, $x = 4{\cdot}3 \times 10^{-4}$, and for the decomposition, $x = 1{\cdot}4 \times 10^{-6}$; these values are also much too small, for the true value, $x = 10^{12}$, cannot be reached. The formation of sulphuryl chloride from sulphur dioxide and chlorine has been measured in glass vessels under the influence of the light from a quartz mercury lamp at 18° and 99° at various concentrations. At the higher temperature, the reaction is of the second order, and gives a good constant. The photochemical reaction does not, however, lead to sulphuryl chloride alone, but many other substances are formed, which cause the velocity constant to decrease. In the case of the decomposition, the presence of these other substances makes it impossible to calculate a velocity constant. An increase in temperature of 80° decreases the velocity of formation by an amount corresponding with a temperature-coefficient of 0·88 per 10°. How far this is to be attributed to a shift in the position of equilibrium or to the disturbing influence of the secondary products (S_2Cl_2, SO_3, $SOCl_2$, $S_2O_5Cl_2$, $S_2O_3Cl_4$) cannot be determined. The velocity of formation of sulphuryl chloride by light is of the same order as that in the presence of carbon in the dark, the effect being the same with a quartz mercury lamp and with a uviol lamp. Sulphuryl bromide is not formed from sulphur dioxide and bromine at temperatures between 106° and 202° in the dark or in the light of a Nernst lamp in the absence of catalysts. Carbonyl bromide is, however, rapidly formed and equilibrium quickly set up, which shows a very large dissociation exists at this point. The equilibrium constants were at 73° $3{\cdot}1 \times 10^3$ mm. mercury, at 181° $1{\cdot}6 \times 10^4$ mm. mercury, from which the heat of formation is calculated, and found to be about 3000 cal. J. F. S.

Influence of Temperature on the Velocity of Solution of Magnesium in Hydrochloric Acid. W. BONSDORFF (*Med. K. vetens. Nobel-institut.*, 1915, **3**, No. 8, 1—34).—The velocity of solution of magnesium has been determined in 0·1, 0·2, 0·3, and 0·4*N*-hydrochloric acid at temperatures from −20° to 75°. Measure-

ments were also made in aqueous alcohol solutions of hydrochloric acid containing 20% and 50% of alcohol. The velocity was determined by measuring the time required for the evolution of 2 c.c. of hydrogen, this being carried out both with and without shaking. It is shown that the velocity increases as the reaction proceeds; it is also increased by increase in the concentration of the acid and by increase in temperature, and is independent of the alcohol concentration. The increase in the velocity is dependent on the velocity itself. Curves and a large number of tables of the results are included in the paper. J. F. S.

Studies on Alcoholysis. I. Dilatometric Determination of the Velocity of Alcoholysis in the Presence of a Large Excess of Alcohol. GOPAL BALKRISHNA KOLHATKAR (T., 1915, **107**, 921—933).—The rate of interchange of radicles in mixtures of esters and alcohols in presence of hydrochloric acid as catalyst has been measured by the dilatometric method. Preliminary experiments showed that the variation in the composition of the mixture is a linear function of the change of the density of the reacting system. The experiments were all made at 30°, with 0·02*N*-hydrochloric acid as catalyst, and, except in one case, the initial ratio of ester to alcohol was 1 : 20. In these circumstances, the alcoholysis proceeds in accordance with the equation for a unimolecular change, and the tabulated values of the unimolecular velocity coefficients are compared with one another.

The coefficients for the alcoholysis of the ethyl esters of acetic, propionic, and *n*-butyric acids by methyl alcohol are in the ratio 100 : 62 : 33·6. The corresponding rates of esterification of the free acids are as 100 : 88·3 : 48·0. For the ethyl esters of acetic, monochloroacetic, trichloroacetic, and benzoic acids the coefficients for alcoholysis are as 100 : 41 : 3·8 : 0·61, whilst the coefficients for the esterification of the acids are as 100 : 35·6 : 0·93 : 0·272. For the *iso*butyl esters of formic and acetic acids, the alcoholysis coefficients are in the ratio 45 : 1, whilst the ratio of the esterification coefficients is 10·8 : 1. These numbers show that the rates of esterification and of alcoholysis follow the same order.

The relative values of the coefficients derived from experiments on the alcoholysis of acetates show that the activities of the alkyl groups may be represented by the series: methyl 100, ethyl 28, *n*-propyl 19, *iso*propyl 3·4, *iso*butyl 16, and *iso*amyl 17.

The ratio of the coefficients for the reactions (1) ethyl ester + methyl alcohol, (2) methyl ester + ethyl alcohol, is almost the same for acetates, propionates, and butyrates, namely, 3·5, 3·8, and 3·7. These numbers show that the relative affinities of the methyl and ethyl groups towards an acyl group are more or less independent of the nature of the acyl group. H. M. D.

Reactivity of the Halogens in Organic Compounds. VIII. Interaction of Alkali Bromoacetates and Bromopropionates in Methyl-alcoholic Solution. GEORGE SENTER and HENRY WOOD (T., 1915, **107**, 1070—1080. Compare T., 1909, **95**, 1827; 1912, **101**, 2534).—The velocity of the reactions between sodium bromo-

acetate and sodium methoxide and sodium bromopropionate and sodium methoxide, both in methyl alcohol solution, and between sodium bromoacetate and sodium methoxide in mixtures of methyl alcohol and water, have been determined at 52·4°. It is shown that the reaction between sodium bromoacetate and sodium methoxide in methyl alcohol is pseudo-bimolecular in character; varying the concentration of the bromoacetate affects the velocity constant to but a slight extent, whereas a change in the concentration of the methoxide affects it strongly in the sense that an increase in concentration produces an increase in the constant. In the case of sodium bromopropionate, the order of reaction comes between that for a unimolecular reaction and that for a bimolecular reaction. In mixtures of water and methyl alcohol, the velocity coefficient is quite constant when calculated for a given experiment by the second order equation. Change in the composition of the solvent produces a change in the velocity constant in the sense that it increases with increasing percentage of water to a maximum, which lies at 50—75% water, and then falls off again (compare Madsen, T., 1913, **103**, 965). J. F. S.

Dynamics of Isomeric Change. Keto-enol Transformation of Cyanoacetic Acid and its Derivatives. HARRY MEDFORTH DAWSON, REGINALD SUGDEN, and ARTHUR TAYLOR (T., 1915, **107**, 1030—1038).—It has been found that sodium cyanoacetate reacts with bromine and iodine in dilute aqueous solution, and that the velocity of the reaction is independent of the concentration of the halogen. From experiments at 0° with solutions in which the sodium cyanoacetate was present in relatively large excess, it was found that the logarithm of the diminution in the concentration of the halogen is a linear function of the time. Assuming that the reaction between the cyanoacetate and the halogen is determined by a preliminary conversion of the keto into the enol form, and that the subsequent reactions in which the enol combines with halogen and halogen acid is set free from the additive compound are of relatively high velocity, and further that the primary isomeric change is catalytically accelerated by the liberated acid, it is shown that the rate at which the halogen may be expected to disappear from the solution is in agreement with the results of experiment. If x denote the concentration of free acid after time t, the relation between x and t may be expressed by the equation $k=(\log x-\log x_0)/t$, in which x_0 is the value of x (obtained by extrapolation) at $t=0$. The value of k from the bromine experiments $=0{\cdot}0242$, and from the experiments with iodine $k=0{\cdot}00685$. The difference in the values of k shows that the velocity is not quite independent of the nature of the halogen, but the difference is not considered sufficiently great to invalidate the hypothesis of isomeric change. It may be due, in part, to the fact that the reaction proceeds to completion with bromine, but not with iodine.

The fact that the apparent initial velocity of the reaction, as measured by x_0, is much greater with bromine than with iodine is attributed to the larger extent to which the bromine is hydrolysed.

With cyanoacetic acid and ethyl cyanoacetate, the halogens react much more quickly, but it is probable that here, also, halogen substitution is preceded by isomeric change. H. M. D.

Catalysis of Hydrogen Peroxide in Homogeneous Media by Acids and Alkalis. Georges Lemoine (*Compt. rend.*, 1915, **161**, 47—51. Compare A., 1912, ii, 747).—The velocity of decomposition of hydrogen peroxide solutions has been determined at 65° by measuring the time required for 0·5, 0·33, 0·25, and 0·1*N* solutions of sulphuric acid and hydrochloric acid to decompose one half of the peroxide present. It is shown that the action of the acids is to retard the decomposition, but although the amount of retardation is greater the greater the concentration of the acid, there is no relationship between concentration of acid and amount of retardation. It has been shown previously (*loc. cit.*) that water acts as a positive catalyst toward hydrogen peroxide, and an attempt to explain the retarding influence of acids is made on the assumption that the acids have a greater affinity for water than hydrogen peroxide has. This is supported by the thermochemical data of Berthelot and Forcrand. Further experiments are made with sodium hydroxide, potassium hydroxide, lithium hydroxide, and sodium peroxide at 65°, 35°, and 9°. These substances all accelerate the decomposition—the hydroxides at about the same rate, the peroxide at about double the rate of the hydroxides. The action of the hydroxides is supposed to be due to the interaction of the hydrogen peroxide with the hydroxide to form a peroxide, which then decomposes with water, thus, $3H_2O + Na_2O_2 = 2NaOH + 2H_2O + \frac{1}{2}O_2$. J. F. S.

Hardening of Oils without Excess Pressure, and with the Application of Nickel and its Compounds as Catalysts. W. Siegmund and W. Suida (*J. pr. Chem.*, 1915, [ii], **91**, 442—468. Compare Bedford and Erdmann, A., 1913, i, 701; this vol., i, 770; Meigen and Bartels, A., 1914, i, 482; Normann and Pungs, this vol., ii, 159).—In order to determine the nature of the catalyst concerned in the hardening of oils by reduction with hydrogen under ordinary pressure in the presence of nickel and its compounds, the authors have investigated the rate of hardening of linseed, cotton, and other unsaturated oils under similar conditions at 230—260° in the presence of the following substances, and have also made a physical and chemical examination of the recovered catalyst when the hardening is practically complete: (1) basic nickel carbonate ($NiCO_3,NiO,4{\cdot}5H_2O$); (2) nickel formate; (3) a mixture of metallic nickel and basic nickel carbonate; (4) voluminous nickelous oxide (Bedford and Erdmann, D.R.-P. 260009); and (5) metallic nickel prepared by reducing the preceding oxide at 280—290°.

They find that the hardening proceeds far more rapidly in the case of the catalysts 1—4, enumerated above, than with metallic nickel, the greatest velocity of reduction being attained when the mixture of basic nickel carbonate and metallic nickel is employed.

It is also shown that under the conditions at which the reduction is carried out, basic nickel carbonate is quantitatively converted into nickelous oxide and carbon dioxide, whilst nickel formate decomposes into carbon monoxide, carbon dioxide, water, hydrogen, and a dark, greyish-black nickel suboxide (D^{20} 5·788) which approximates in composition to the formula Ni_3O, has no electrical conductivity, does not show the nickel carbonyl reaction at 30—90°, and therefore is free from metallic nickel.

In view of the greater velocity of reduction in the presence of the oxy-compounds of nickel, the authors agree with Ipatiev that water plays a part in the reduction process. Further, the superiority of the catalysts 1—3 over nickelous oxide is attributed to the greater ease with which these substances are converted into a nickel suboxide.

An examination of the catalysts 1—4, after recovery from the hardening process, shows that they are practically free from metallic nickel, provided that the reduction has not been carried too far; in only one instance in which nickelous oxide was used and the hardening carried to completion did the recovered catalyst contain an appreciable amount (2·5%) of the free metal. They form blackish-grey powders, having a density varying from 2·809—5·431 at 17·5°, and possess a very small electrical conductivity. The composition is nearly the same in all cases, carbon and hydrogen being present in addition to oxygen. The carbon content is due to the presence of organic nickel salts derived from the free acid of the original oil, and on the assumption that this acid is palmitic acid, the composition of the recovered catalysts corresponds approximately with the formula Ni_2O.

Although metallic nickel could not be detected with certainty from the analysis, density, or electrical conductivity, the authors are of the opinion that traces of the metal are present in the recovered catalyst, but not to the extent stated by Normann and Pungs.

Meigen and Bartels (*loc. cit.*), in common with the last-named authors, attribute the catalytic effect of the oxide and oxy-salts of nickel to the presence of this small amount of the free metal. That this view is incorrect is shown by the fact that the hardening proceeds at a far greater rate with nickelous oxide as the initial catalyst than with metallic nickel. Further, although the addition of metallic nickel to basic nickel carbonate results in a catalytic activity superior to that of either of the two substances alone, the free metal cannot be detected in the recovered catalyst, and therefore must have been converted into oxide during the reduction of the oil. Only when the fat has been completely hardened does reduction to metallic nickel occur.

From the above results, the conclusion is drawn that the real catalyst concerned in the hardening of oils in the presence of nickelous oxide or oxy-salts of nickel is one of the lower oxides, probably Ni_2O, which, in the presence of water simultaneously formed in the reaction, undergoes alternate oxidation to nickelous oxide and reduction to the suboxide, the unsaturated character of

the oil preventing the complete reduction to the metal; metallic nickel, if formed at all, is produced to only a very small extent, and takes no further part in the hardening process. F. B.

The Shape of Molecules. II. THE. SVEDBERG (*Arkiv. Kem. Min. Geol.*, 1914, **5**, No. 11, 1—6).—In former articles the author has dealt qualitatively (A., 1914, ii, 97) and quantitatively (*Arkiv. Matematik.*, 1913, **9**, Nos. 9 and 21) with a method which may be used for ascertaining the dis-symmetry of the molecules, and in the present paper the results of certain series of measurements are given. Using the anisotropic substance azoxyphenetole as solvent, and measuring the electrical conductivity of a dissolved electrolyte or the velocity of diffusion of a dissolved non-electrolyte in directions parallel and at right angles to the direction of the axes of the solvent molecules, it is possible to calculate the ratio between the two axes of the solute molecules, assuming that these molecules consist of rotation elipsoids; the measurements are carried out at various temperatures below that of the clearing point of the solvent.

Using phenol, *o*-nitrophenol, quinol, and pyrogallol as solutes, the axial ratio of the benzene molecules was found to be 1·63. With β-naphthol and sodium α-dinitronaphthol as solutes, the axial ratio for the naphthalene molecule was calculated to be 2·93. If it is assumed, among other things, that the benzene and naphthalene molecules are elipsoidal in form, and further that their minor axes, *b* and *c*, are of the same length in the two molecules, it can be calculated that the relative lengths of their major axes are 1 : 1·79, that is, numbers are obtained which are in qualitative agreement with the ratio 1·63 : 2·93 of the numbers given above.

T. S. P.

Inorganic Chemistry.

Purification of Commercial Hydrochloric Acid. A. COIGNARD (*Ann. Chim. Anal.*, 1915, **20**, 145—146).—A review of various laboratory methods proposed for the purification of hydrochloric acid. Simple distillation is ineffective. Houzeau's process, in which potassium chlorate is added previous to distillation, has the disadvantage that the distillate is contaminated with chlorine, and if distillation is carried too far, arsenic acid is decomposed into arsenious chloride and chlorine, and arsenic will be found in the distillate. Removal of the arsenic previous to distillation by the addition of stannous chloride, as recommended by Bettendorf, is preferable. After keeping for twenty-four hours, the decanted liquid, to which a little sodium chloride may be added if much sulphuric acid is present, is distilled until the residue is quite

syrupy. Volatilisation of tin as stannic chloride can only take place if arsenic has not been completely eliminated before distillation. Duflos' method, although giving a weaker acid, is otherwise free from all objection. After dilution to D 1·13, and adding a little potassium chlorate if sulphurous acid is present, a few strips of copper are added, and the liquid is maintained at 30° for twenty-four hours. After cleaning the copper, the treatment is repeated, and the decanted liquid eventually distilled over copper. The above processes also serve to remove antimony, except that with very impure acids traces may pass over into the distillate if Bettendorf's method is used. G. F. M.

Sulphites, Thiosulphates, and Polythionates. II. A. SANDER (*Zeitsch. angew. Chem.*, 1915, **28**, 273—277. Compare this vol., ii, 161).—The author reviews the various methods given for the preparation of tetrathionates. None of the methods gives a pure product, and it is shown that this is due primarily to the fact that the presence of any thiosulphate accelerates the decomposition of the tetrathionate, and in the methods generally used thiosulphate is always present. The pure sodium and potassium tetrathionates can be made as follows, the method being such that thiosulphate is not allowed to remain in the presence of tetrathionate. To a cooled solution of 26 grams of iodine in alcohol is added, drop by drop, a saturated solution in water of 50 grams of sodium thiosulphate or 39·5 grams of potassium thiosulphate. The tetrathionate, which separates out as it is formed, is collected, and washed with alcohol until it is free from iodine and iodide, dissolved in a little water, and again precipitated by alcohol. After drying over sulphuric acid, it can be kept for many months without undergoing decomposition.

The salts thus obtained were shown to be pure by analysis according to four different methods, namely: (1) calcination; (2) oxidation with mercuric chloride (compare this vol., ii, 161); (3) oxidation with bromine; and (4) reduction with nascent hydrogen and estimation of the hydrogen sulphide formed. Qualitatively, it was shown not to contain the least traces of either sulphate or thiosulphate.

Aqueous solutions of tetrathionates slowly decompose, primarily according to the equation $K_2S_4O_6=K_2SO_4+SO_2+2S$, but some thiosulphate is formed at the same time. The decomposition is so slow, however, that a tenth- or fiftieth-normal solution can be gently boiled for an hour without undergoing decomposition. In the presence of thiosulphates, however, it readily decomposes. According to Feld (A., 1913, ii, 617), this decomposition is due to the reaction $Na_2S_4O_6+2Na_2S_2O_3=3Na_2SO_4+5S$, but the author shows that this is incorrect, the action of the thiosulphate being purely catalytic. T. S. P.

Tetrathionates. F. CALZOLARI (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 921—925).—Tetrathionic acid, $OH\cdot SO_2\cdot S\cdot S\cdot SO_2\cdot OH$, and persulphuric acid, $OH\cdot SO_2\cdot O\cdot O\cdot SO_2\cdot OH$, not only possess similar

structure, but exhibit various analogies. The author finds that the tetrathionates form, with ammonia, pyridine and hexamethylenetetramine, compounds corresponding in composition, external form, and solubility with those given by the persulphates (A., 1911, ii, 889); crystallographic resemblance has not been traced, since the additive compounds of the persulphates have not been obtained in measurable crystals. Compounds of hexamethylenetetramine with magnesium, cobalt and nickel tetrathionates, like those with the corresponding persulphates, contain $8H_2O$. The following compounds have been prepared.

Ammine tetrathionates: *zinc*, $ZnS_4O_6,4NH_3$, transparent, colourless crystals; *nickel*, $NiS_4O_6,6NH_3$, microscopic, lilac prisms.

Pyridine tetrathionates: *zinc*, $ZnS_4O_6,4C_5H_5N$, colourless, prismatic crystals; *cadmium*, $CdS_4O_6,4C_5H_5N$, similar to the preceding compound; *copper*, $CuS_4O_6,4C_5H_5N$, moderately stable, dark blue, acicular crystals; *nickel*, $NiS_4O_6,4C_5H_5N$, blue, acicular crystals; *cobalt*, $CoS_4O_6,4C_5H_5N$, violet-red, microscopic needles.

Hexamethylenetetramine tetrathionates, $MS_4O_6,8H_2O,2C_6H_{12}N_4$, stable in the air and soluble in cold water: *magnesium*, colourless, transparent prisms; *nickel*, pale green, transparent prisms; the *cobalt* compound, which forms red prisms, dissolves in the solid state in the magnesium and nickel compounds. T. H. P.

The Preparation of Sodium Selenate and Selenic Acid. JULIUS MEYER and KARL HEIDER (*Ber.*, 1915, **48**, 1154—1158).—An incomplete investigation of the oxidation of selenium dioxide by sodium peroxide, hydrogen peroxide, and anodic electrolysis; the first method gave most satisfactory results.

Fusion with rather more than the theoretical amount of sodium peroxide converted selenium dioxide into a mass the solution of which, after treatment with carbon dioxide, yielded on evaporation crystals consisting of approximately 80% sodium selenate.

When warmed with rather more than the theoretical quantity of 30% hydrogen peroxide solution on a water-bath, selenium dioxide passed into solution, and a single evaporation yielded a solution containing 47% of the original selenium as selenic acid.

Electrolytic oxidation was effected in nitric acid solution (D 1·4) with a platinum foil anode at 70—80°. Curves are given representing the rate of formation of the selenic acid, and it is shown that the formed selenic acid exerts an autocatalytic effect on the oxidation of the remaining dioxide (compare Glauser, A., 1907, ii, 614). D. F. T.

[Vapour] Tension Lines of the System Phosphorus. IV. A. SMITS and S. C. BOKHORST (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 106—116. Compare this vol., ii, 49, 164).—In the further investigation of the vapour-pressure curve of liquid white phosphorus, measurements of the boiling point at different pressures have been made with the aid of the apparatus described by Smith (A., 1910, ii, 687, 1037). The vapour pressures of liquid white phosphorus between 160° and 360° are represented quite

satisfactorily by the equation $T\log p = -Q/R + CT$, in which Q, the molecular heat of vaporisation, is equal to 12·17 Cal. It has been shown previously that the vapour pressures of liquid violet phosphorus between 510° and 630° are similarly in agreement with this equation if $Q = 9·96$. On the assumption that these quantities have reference to the vaporisation, and that the difference is due to the linear variation of the heat of vaporisation with the temperature, according to $Q_r = Q_0 + \alpha T$, it follows that $dQ/dr = -0·007106$. The vapour-pressure equation then assumes the form $\log p = -Q_0/RT - 3·59\log T + C$, according to which $T\log p + 3·59T\log T$ is a linear function of the temperature. The experimental data are found to satisfy this requirement.

The experimental data when applied to the evaluation of C and Q_0 gave $C = 37·62$ and $Q_0 = 16·35$ Cal., from which it follows that the vapour pressure for liquid white phosphorus between 160° and 360°, and for liquid violet phosphorus between 510° and 630°, can be represented by the equation

$$T\log p + 3·59T\log T = 37·62T - 8257.$$

The above results lead to the conclusion that liquid white phosphorus must be regarded as supercooled liquid violet phosphorus.

H. M. D.

Phosphoric Acid as a Monobasic and Dibasic Acid. I. M. Kolthoff (*Chem. Weekblad*, 1915, **12**, 644—653).—The equilibrium $H^{\cdot} + HPO_4'' \rightleftharpoons H_2PO_4'$ is endothermic from left to right. Addition of sodium chloride displaces the equilibrium from right to left. With dimethylaminoazobenzene as indicator, phosphoric acid can be accurately titrated as a monobasic acid, and with phenolphthalein in presence of an equal volume of a saturated solution of sodium chloride as a dibasic acid. A. J. W.

Behaviour of Phosphoric Acid with Calcium Hydroxide. I. M. Kolthoff (*Chem. Weekblad*, 1915, **12**, 662—666).—Titration of phosphoric acid with lime-water, using dimethylaminoazobenzene as indicator, neutralises one equivalent of the acid. Inversely, primary calcium phosphate can be prepared by titrating lime-water with phosphoric acid in presence of the same indicator. Secondary calcium phosphate cannot be obtained by this method.

A. J. W.

Compounds of Arsenious Oxide. II. F. A. H. Schreinemakers and (Miss) W. C. de Baat (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 126—132. Compare this vol., ii, 256).—The question of the formation of compounds by the combination of arsenious oxide with the alkali metal chlorides has been investigated by a study of the equilibrium relations in the ternary systems which these form with water as the third component. The composition of the saturated solutions which are formed at 30°, and also that of the coexisting solid phases, was determined. The results obtained show that sodium chloride does not form a compound with arsenious oxide, that ammonium chloride forms a compound of the composi-

tion NH_4Cl,As_2O_3, and that potassium chloride yields the compound $5KCl,6As_2O_3$. The compounds are decomposed by water, with separation of arsenious oxide. H. M. D.

A Reaction of Diamond. LUIGI COLOMBA (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 1137—1141).—Moissan (A., 1893, ii, 319) found that when diamond is heated with a fused mixture of alkali carbonates, it undergoes complete transformation into carbon monoxide. The author shows that this change consists of a reduction by the diamond of the carbon dioxide resulting from the decomposition of the alkali carbonate: $C + CO_2 = 2CO$. T. H. P.

Thermal Study of the Carbonisation Process. HAROLD HOLLINGS and JOHN WILLIAM COBB (T., 1915, **107**, 1106—1115).—The inconclusive nature of the evidence supporting the view that the carbonisation of coal is an exothermic process has led the authors to carry out a series of thermal measurements in connexion with the carbonisation of coal and certain other substances.

The method employed consisted in heating simultaneously under the same conditions a carbonising coal and a coke which could be regarded as chemically and thermally inert, and observing, by means of a differential arrangement of thermocouples, the extent to which the temperature of the coal became higher or lower than that of the coke at different stages of the carbonisation process. Complications arising from the secondary decomposition of volatile distillation products were minimised by using a small quantity of coal and removing the products by a stream of nitrogen. Heating curves were also determined for coal extracts in order to ascertain how far it was possible to trace characteristics of the curve for coal to the influence of constituents of the coal itself. In addition to different types of coal, cellulose, dehydrated cellulose, and lignite were examined in order to trace the possible influence of degradation products of cellulose still present in the coals.

Comparison of the results with chemical data suggests the following correlation of chemical and thermal stages in carbonisation: (1) Below 400°, cellulose shows a strongly exothermic reaction, beginning at 345°. This is much feebler in dehydrated cellulose and lignite, and absent in the coals, and is presumably connected with the loss of hydroxyl groups and molecular condensation in the residue. (2) 400—600°; in this interval, the characteristic differences in the types of coal are exhibited. Oils, unsaturated hydrocarbons, higher paraffins, and oxygenated compounds are evolved, and the thermal phenomena vary with the quality of the coal. (3) 600—800°; methane is evolved, and marked exothermicity is shown by all the coals examined. If the carbonisation is on the whole exothermic, it is probable that the chief cause is to be found in the exothermic character of this stage. (4) Above 800°. This is the stage where hydrogen is the chief product, and in thermal character it is either neutral or slightly endothermic.

Thermal phenomena at low temperatures are most marked with cellulose and coals containing much oxygen, whilst high-tempera-

ture phenomena are most marked with anthracite and coals of low oxygen content. H. M. D.

Boyle's Views on the Calcination of Metals. Ernst Bloch (*Chem. Zeit.*, 1915, **39**, 481—482).—Historical. G. F. M.

Thermal Analysis of Mixtures of Alkali Hydroxides and Haloids. II. Sodium Compounds. Giuseppe Scarpa (*Atti R. Accad. Lincei*, 1915, [v]. **24**, i, 955—961).—The systems NaOH–NaF, NaOH–NaCl, NaOH–NaBr, and NaOH–NaI were investigated in a manner similar to that used with the corresponding mixtures of potassium compounds (this vol., ii, 448). The sodium hydroxide employed contained 97·46% NaOH, 1·64% Na_2CO_3, and 0·9% H_2O, and had m. p. 310°, and solidification temperature 290°. Von Hevesy (A., 1910, ii, 835) gave 318·4° and 299·5° respectively, and Neumann and Bergve (A., 1914, ii, 422) found the solidification point 300°.

For sodium fluoride, the author finds m. p. 1005°. Plato (A., 1907, ii, 239) gave 992°, Kurnakov and Schemtschuschni (A., 1906, ii, 443) 997, Ruff and Plato (A., 1903, ii, 588) 980°, and Puschin and Baskov (A., 1913, ii, 319) 1040°. The system NaOH–NaF yields mixed crystals with a miscibility gap. The curve of primary crystallisation lies between the solidification points of the components, with a slight change in direction at 90 mol. % NaOH.

For sodium chloride, m. p. 806° is found. White (A., 1909, ii, 970) gave 800°, Arndt (A., 1906, ii, 418) 805°, Ruff and Plato (*loc. cit.*) 820°, Hüttner and Tammann (A., 1905, ii, 229) 810°, Menge (A., 1911, ii, 982) 803°, Truthe (A., 1912, i, 612) and Sandonnini (A., 1911, ii, 606) 806°. The system NaOH–NaCl is analogous to the preceding, two types of solid solution being formed with a miscibility gap. The curve of primary crystallisation exhibits a marked angle at 350° and about 75 mol. % NaOH.

For sodium bromide, the author finds the solidification point 776°. Ruff and Plato (*loc. cit.*) gave 765°, Kurnakov and Schemtschuschni (*loc. cit.*) 768°, and McCrae (A., 1895, ii, 339) 761°. Sodium hydroxide and bromide are completely miscible in the fused state, the curve of primary crystallisation of the system consisting of two branches, which intersect at the eutectic point, about 260°. No appreciable formation of solid solutions occurs.

For sodium iodide, the author finds m. p. 665°. Ruff and Plato (*loc. cit.*) gave 650°, Hüttner and Tammann (*loc. cit.*) 664°, and Kurnakov and Schemtschuschni (*loc. cit.*) 660°. The system NaOH–NaI forms a compound, probably 2NaOH,3NaI, which decomposes on fusion.

Leaving aside the fluorides, which approach in behaviour the corresponding hydroxides, with both the sodium and the potassium compounds, the solubility in the solid state decreases from the chlorides to the bromides to the iodides, that is, as the electro-affinity of the anion diminishes. That NaOH–NaBr gives a simple eutectic, and NaOH–NaI a compound, whereas KOH–KBr forms solid solutions with a miscibility gap, and KOH–KI a simple

eutectic, is probably due to the fact that the electro-affinity of Na^+ is less than that of K^+. T. H. P.

Allotropy of Sodium. I. ERNST COHEN and S. WOLFF (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 91—98. Compare this vol., ii, 83).—In the further investigation of the relationships between α- and β-sodium, experiments have been made with a dilatometer containing about 400 c.c. of sodium and a small quantity of petroleum as index fluid. The dilatometer readings show that the rapidly cooled metal occupies a larger volume than the solid which is obtained when the fused metal is allowed to cool slowly. The β-modification is therefore less dense than the α-form, although the difference is very small. At temperatures just below the melting point (97·22°), the β-form is transformed into the α-form with measurable velocity. The change takes place with maximum velocity about 2° below the melting point. From these observations, the conclusion is drawn that sodium is monotropic.

Under exactly similar conditions, liquid sodium is formed more rapidly from the β-form than from the α-form, and from this it would seem that the change $\beta \longrightarrow \alpha$ is accompanied by the development of heat. H. M. D.

Solubility of Glass in Water. R. (FRH.) VON WALTHER (*J. pr. Chem.*, 1915, [ii], **91**, 332).—The solubility of glass in water can be readily demonstrated by boiling water containing a little alizarin in an ordinary flask until the solution acquires a reddish, or even violet, colour, and then titrating with $N/100$-sulphuric acid. F. B.

Mixed Salts of Calcium and Magnesium Carbonates. KURT SCHMIDT (*Jahrb. Min.*, 1915, i, *Ref.* 169—170; from *Inaug.-Diss. Jena*, 1913, 1—49).—Working on the lines suggested by Linck (A., 1911, ii, 294; compare 1913, ii, 959) with solutions of calcium and magnesium chlorides and ammonium sesquicarbonate, the effects of the excess of one or other of these solutions, their concentration, and of temperature on the nature of the deposited calcium–magnesium carbonate has been studied in minute detail. L. J. S.

An Allotropic Modification of Lead. HANS HELLER (*Zeitsch. physikal. Chem.*, 1915, **89**, 761—762).—When pure lead is allowed to remain in an acidified solution of lead acetate for several days it becomes brittle, and may be powdered. This is an entirely new form of lead, and is designated "grey lead." The same transformation occurs in lead nitrate solutions, and also in lead chloride solution, but in the latter case much more slowly. The change is always more rapid if a small quantity of nitric acid is present. There is no change if lead is immersed in acetic acid, nitric acid, or sodium acetate solutions, thus showing that the transition is due to the presence of lead ions. These results, and also the nature of the product, have been confirmed by Cohen and Heldermann (this vol. ii, 456). J. F. S.

The Atomic Weight of "Uranium-lead." O. HÖNIGSCHMID and ST. HOROVITZ (*Monatsh.*, 1915, **36**, 355—380. Compare A., 1914, ii, 653).—Preliminary determinations having shown that the lead from the residues of Joachimsthal pitchblende, which contained the lead in the raw sulphuric acid used, had an atomic weight of 206·73, that of the lead from 20 kilos. of selected purest Joachimsthal pitchblende, extracted by the use of pure reagents, was determined, and found to be 206·405. A crystallised uranium ore from an old primary geological formation in Morogoro, in German East Africa, analysed by Marckwald, and specially pure, gave a lead with the value 206·046 ± 0·014 for the atomic weight. That from bröggerite from Moos, Norway, a very old primary mineral almost free from contamination with heavy metals, and containing 79% U_3O_8, 4·5% ThO_2, and 9·5% PbO, gave the value 206·063 ± 0·008. In control of the methods employed, a determination of the atomic weight of common lead gave the value 207·180 ± 0·006. A comparison of the arc and spark spectra of the lead of atomic weight 206·046 and common lead showed absolute identity. Full details are given of the preparation and purification of the lead from the various sources, of the reagents used, and the carrying out of the determinations, which followed the method of Baxter and Wilson, the ratios $PbCl_2$: 2AgCl and $PbCl_2$: 2Ag being found. The crude lead sulphate obtained was dissolved in ammoniacal ammonium acetate, and precipitated as sulphide by ammonium sulphide. After conversion into nitrate, it was purified by solution in water and precipitation with nitric acid, being then converted into chloride, and crystallised five times from water. In some cases the lead chloride was distilled in a quartz apparatus. F. S.

Copper, Nickel, and Cobalt Alloys. M. WAEHLERT (*Chem. Zentr.*, 1914, ii, 919—920; from *Oesterr. Zeitsch. Berg. Hutten-wesen*, 1914, **62**, 341—346, 357—361, 374—378, 392—395, 406—410).—A thermal, magnetometric, and mechanical investigation of the binary systems Cu–Co, Ni–Co, and the tertiary system Ni–Cu–Co. Electrolytic copper, electrolytic nickel, and cobalt prepared by reduction of cobaltous oxide with hydrogen, were employed, and the alloys were prepared in a tube furnace in porcelain reagent tubes (under a layer of borax glass in the case of the nickel and copper alloys). The magnetometric measurements were made with a special magnetometer, described in detail in the original paper. The statements of Ruer and Kaneko with regard to nickel–cobalt (A., 1912, ii, 1059), and of Lahmen concerning copper–cobalt alloys (A., 1908, ii, 187), were, in the main, confirmed. In the ternary system Cu–Ni–Co the alloys consisted of ternary mixed crystals; ternary compounds were not present. With a definite copper content, the hardest alloy is obtained when cobalt and nickel are added in equal proportions. The alloys are, in general, stable towards sulphuric acid, but are all attacked by nitric acid. The most resistant is monel metal (1 part copper + 4 parts nickel), which is accordingly of much value in automobile and shipbuild-

ing. Addition of cobalt diminishes the power of resistance to acids. The original papers are illustrated with numerous tables and diagrams. G. F. M.

Position of the Elements of the Rare Earths in the Periodic System. R. J. MEYER (*Chem. Zentr.*, 1914, ii, 816—817; from *Naturwiss*, 1914, **2**, 781—787).—A theoretical paper dealing with the irregularities of the periodic system, and the position and properties of the rare earths. Whilst cerium finds a place in the fourth group, the other cerium and ytterbium earths present difficulties. The author places them in the third group, and divides them into three sub-groups, each of five elements (La to Eu, Gd to Er, Tu to Lu, two still unknown elements having places between Tu and Yb). These sub-groups form a miniature periodic system for themselves, in which all the characteristics of the main system are reproduced. G. F. M.

Cause of the Red Coloration Sometimes Observed in the Dissolution of Thomas Slags in Sulphuric Acid. HUGO DITZ (*J. pr. Chem.*, 1915, [ii], **91**, 507—520).—Although Thomas slags usually give bluish-green solutions when heated with sulphuric acid, samples are occasionally encountered which give a red coloration. Since these red solutions resemble those obtained by dissolving manganese dioxide in phosphoric acid, in that the colour is discharged by dilution with water and by the addition of ferrous sulphate, sodium sulphite, and hydrogen peroxide, the conclusion is drawn that the red coloration is due to the presence of a higher oxide of manganese in the slag.

Further evidence in support of this view is furnished by the evolution of chlorine on treatment with hydrochloric acid, and by the development of a red solution when a slag, which showed the usual bluish-green colour, was mixed with manganese dioxide or potassium permanganate prior to its dissolution in sulphuric acid, the dioxide or permanganate being added in sufficient amount to destroy the reducing substances present in the slag.

That the red coloration is independent of the other constituents of the slag is shown by the fact that a similar coloration is produced by a mixture of pure calcium phosphate and manganese dioxide. Slags which do not yield red solutions may be made to do so by heating them strongly whilst exposed to air. It is therefore probable that the formation of slags giving red solutions is due to atmospheric oxidation during slow cooling, and will be favoured by a high manganese content, the presence of free lime, and the absence of large amounts of ferrous oxide and other oxidisable substances. F. B.

The Reaction between Cobaltous Oxide and Aluminium Oxide at High Temperatures. J. ARVID HEDVALL (*Arkiv. Kem. Min. Geol.*, 1914, **5**, No. 16, 1—10).—Fusions of cobaltous oxide and alumina in varying proportions have been made at 1100° and 1300—1400° in the presence of potassium chloride as a flux.

When the cobalt oxide is in excess, the resulting product can be obtained pure by treatment with water to remove the flux and with hydrochloric acid to remove the excess of cobalt oxide. If alumina is in excess, the pure product cannot be obtained.

The results show that at 1100° the blue aluminate, of the composition CoO,Al_2O_3, is formed. At temperatures above 1100°, a hitherto unknown *green aluminate*, $4CoO,3Al_2O_3$, is formed. The analytical figures for this green compound are only in approximate agreement with the formula given, but the small deviations observed may be accounted for by small quantities of cobalt oxide remaining dissolved in the compound.

Neither aluminate was obtained in the form of well-developed crystals. The blue compound has D^{18} 4·37, and the green compound D^{18} 4·80. T. S. P.

Metallo-compounds of Cobalt and Nickel. Spencer Umfreville Pickering (T., 1915, **107**, 942—954).—The present paper deals with experiments undertaken to ascertain whether the metals of the iron group, cobalt and nickel, form metallo-compounds similar to the cupri-compounds (T., 1911, **99**, 800; 1910, **98**, 1841; 1912, **101**, 176; 1913, **103**, 1361). It is shown that both nickel and cobalt form compounds closely analogous to the cupri-compounds, which are characterised by great solubility and depth of colour, and by the fact that the metal is present as a complex anion, which migrates to the anode on electrolysis. These compounds have been obtained as double carbonates and citrates, and as tartrates, racemates, malates, citrates, and glycerates. These compounds can all be obtained in solution by: (1) the interaction of the respective acids on carbonates of the metals; (2) double decomposition between the potassium salt of the acid in question and the chloride of the metal; or (3) the action of potassium hydroxide on the normal salts. When the solutions are treated with alcohol, the metallo-compound is, in most cases, precipitated. The colour intensity of solutions of inorganic salts is not affected by dilution, except in the case of very concentrated solutions of cobalt, but the colour intensity of organic salts decreases on dilution. In solution, the metallo-compounds gradually change into the corresponding less soluble normal salts, which crystallise out. Several cases are found where the compounds can exist in the form of jellies, and in the case of nickel the normal salts can also exist as jellies. Two metameric forms of normal cobalt racemate have been prepared. J. F. S.

Metallo-compounds in Solution. Spencer Umfreville Pickering (T., 1915, **107**, 955—959. Compare preceding abstract).—When aqueous solutions of metallo-compounds are evaporated, there separates either crystals of the normal salt, or a glass consisting of the metallo-compound, or both substances. The metallo-compounds obtained as emulsions are soluble to an almost indefinitely large extent, and on evaporation of the solutions thus obtained they separate as either a glass or as scales. Both forms are

excessively soluble, but often, particularly in the case of the scaly form, only slowly soluble. The double citrate of copper and potassium separates from solution as a clear, blue glass, along with white crystal rosettes, and on removing the rosettes, redissolving the glass, and evaporating, both forms are again produced. The mixed residue is stable in dry air, but in moist air it deliquesces, and all passes over into the crystalline normal salt, which then becomes dry. A list of the copper metallo-compounds is given, showing the intensity of colour and the nature of the deposit on evaporation. Scaly residues were obtained with the citrate, malate, and glycerate of nickel, the citrate and glycerate of cobalt, and the potassium cobalt citrate; with the exception of the glycerates, the whole of these compounds were converted into crystals by repeated solution and recrystallisation. J. F. S.

The Reaction between Stannic Oxide and Cobaltous Oxide at High Temperatures. J. ARVID HEDVALL (*Arkiv. Kem. Min. Geol.*, 1914, **5**, No. 18, 1—7).—Mixtures of stannic oxide and cobaltous oxide in varying proportions were fused at 1100° and 1300—1400°, using potassium chloride as a flux. After removal of the potassium chloride by means of water, the stannate formed can be dissolved out from any excess of stannic oxide by treatment with warm, dilute, hydrochloric acid. Analyses of the solutions thus obtained indicate the formation of *cobalt orthostannate*, Co_2SnO_4. When cobalt oxide was in excess, no method of separating it from the orthostannate could be found.

Pure cobalt orthostannate is dark green in colour, and has D^{18} 6·30. It could not be obtained in the form of large crystals. If excess of stannic oxide is present in the fusion, the colour becomes more and more blue as the dilution with stannic oxide is increased.

Cobalt metastannate, made by precipitation of a solution of potassium metastannate with a cobalt salt, is changed into the orthostannate on strongly heating; the colour is then a bright, greenish-blue, because of the excess of stannic oxide present.

T. S. P.

Mineralogical Chemistry.

The Mineralogy of Sweden. III. GUST. FLINK (*Arkiv. Kem. Min. Geol.*, 1914, **5**, No. 10, 1—273).—An account is given of the distribution in Sweden of the following minerals: kobellite, calc spar, magnesite, petalite, felspars, enstatite–bronzite–hypersthenes, pyroxene, spodumene, wollastonite, pectolite, rhodonite, babingtonite, amphibole, anthophyllite–gedrite, and hornblende. Full crystallographic and mineralogical details are given. T. S. P.

Enclosures of Anthraxolite in Igneous Rocks in the Crimea. V. V. Arshinov (*Jahrb. Min.*, 1915, i, Ref. 186—187; from *Petrogr. Inst. "Lithogaea," Moscow, Publication* No. 4, 1914, 1—15).—The name anthraxolite is limited to material having the physical characters and chemical composition of anthracite, but related genetically to the bitumens. It has probably been formed by the oxidation and polymerisation of gaseous and liquid hydrocarbons, which have arisen as distillation products at the contact of igneous intrusions into carbonaceous clay-slates. Such material is found as shining black nodules (1—2 cm. diam.) in keratophyre at Cape Parthenit (anal. I and II), and in an igneous rock on Mt. Karaúl-chaya, near the village of Lemeny (III, IV). The material is insoluble in carbon disulphide.

	C.	H.	O.	S.	N.	H_2O.	Ash.	Sp. gr.	Hardness.
I.	90·22	3·51	3·32	0·44	0·77	1·20	0·54	1·40	3—3½
II.	91·82	3·57	3·38	0·45	0·78	—	—	—	—
III.	91·35	3·74		3·36		1·33	0·22	1·38	2–2½
IV.	92·79	3·80	3·41	—	—	—	—	—	—

L. J. S.

Decomposition of Smaltite and Löllingite by Oxidation in the Air. A. Beutell and Fr. Lorenz (*Centr. Min.*, 1915, 359—373. Compare A., 1911, ii, 485, 728, 1094; this vol., 356).—Smaltite from Riechelsdorf, Hesse, gave analyses I—III, corresponding with the ratios Co: As = 1: 2·85, 1: 2·87, and 1: 2·53 respectively. When heated in a vacuum up to 600°, arsenic is lost from this material, leaving a residue of CoAs. By the slow oxidation of the powdered mineral in dilute hydrochloric acid in the presence of air, there passes into solution, first, Co_2As_5, and afterwards $CoAs_2$, leaving a residue of $CoAs_2$.

	Co.	Ni.	Fe.	As.	Sb.	Bi.	S.	Insol.	Total.
I.	10·98	9·79	0·75	77·10	0·47	—	0·39	0·56	100·04
II.	10·23	10·41	0·78	77·32	0·62	—	0·42	0·13	99·91
III.	10·88	9·41	2·78	72·97	—	1·31	1·70	0·58	99·63
IV.	—	—	29·05	68·21	—	—	1·32	1·21	99·79
V.	—	—	28·86	68·38	—	—	1·32	1·21	99·77

Löllingite from Reichenstein, in Silesia, gave IV and V, corresponding with Fe: As = 1: 1·83 and 1: 1·85 respectively. In dilute hydrochloric acid with air, Fe_2As_3 passes into solution, leaving a residue of $FeAs_2$. L. J. S.

Opal and Associated Minerals from Govt. Kherson. P. Grischtschinsky (*Jahrb. Min.*, 1915, i, Ref. 168; from *Mém. Soc. Natur. Kiev*, 1914, **23**, 113—115).—A pelikanite-granite near the village Novo-Michailovka contains veins of opal 2—3 cm. in thickness. Analysis I is of milk-white opal, II of yellow opal, and III of red opal. Under the microscope, particles of opal are seen to be enveloped in chalcedony, and to enclose grains of quartz.

Analysis IV is of material which has been more completely converted into chalcedony.

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	H_2O.	Total.
I.	90·58	0·17	0·41	0·22	trace	7·92	99·30
II.	91·56	0·31	0·67	0·10	trace	6·68	99·32
III.	90·21	0·25	2·32	0·11	—	7·05	99·94
IV.	95·30	1·01		—	—	3·55	99·86

L. J. S.

Tachhydrite in the Potash-salt Deposits of the Mansfeld Basin. P. KLING (*Centr. Min.*, 1915, 11—17, 44—50).—Tachhydrite occurs in abundance in the upper carnallite region in the south-eastern portion of the basin. It forms an intimate intermixture with carnallite, sylvite, and halite. It is of secondary origin, and has resulted by the action of magnesium chloride solutions on anhydrite. Synthetical experiments show that crystals of tachhydrite can take into solid solution small quantities of ferrous chloride, but none of ferric chloride. This explains the yellow colour of the natural mineral, the ferrous chloride being then partly oxidised to hæmatite. L. J. S.

Modifications of Witherite when Heated. J. SAMOILOV (*Centr. Min.*, 1915, 161—163).—The heating curve of witherite and of precipitated barium carbonate shows two breaks, one, previously observed, at about 800°, and a second, much less pronounced, at about 970°. These breaks correspond with a change in state from witherite to α-witherite, and from α-witherite to β-witherite. These changes are reversible, but, owing to over-cooling, the transformation temperatures are about 30° lower on the cooling curve. Strontianite shows only one transformation temperature, namely, at about 875° on the cooling curve. L. J. S.

The Minerals of the St. Kreuz (Alsace) Mineral-veins. R. KRAEMER (*Jahrb. Min.*, 1915, i, Ref. 331—333; from *Mitt. Geol. Landesanstalt Elsass-Lothringen*, 1914, 8, 449—509).—A detailed account is given of the various mineral species and their paragenesis. The following analyses are given of chalybite (I), ankerite (II), and pearlspar (III and IV).

	$CaCO_3$.	$MgCO_3$.	$FeCO_3$.	$MnCO_3$.	Insol.	Total.	Sp. gr.
I.	7·48	7·34	79·83	4·67	1·11	100·43	3·63
II.	40·39	4·32	48·44	2·45	2·39	97·99	3·19
III.	56·58	16·32	26·81	0·19	0·10	100·00	2·77
IV.	61·70	16·34	20·30	—	0·09	98·43	2·99

Analysis of pitticite gave:

$FeAsO_4$.	$Fe_2(SO_4)_3$.	$Fe(OH)_3$.	H_2O.	Total.
41·23	6·15	25·54	27·08	100·00

L. J. S.

Aurichalcite from Japan. Takeo Katō (*Jahrb. Min.*, 1915, i, Ref. 171; from *Journ. Geol. Soc. Tokyo*, 1913, **20**, 9—11).—Earthy, scaly, and acicular aurichalcite lines cavities in brown calamine from the Tsuzuragahayama mine in prov. Nagato. D^{18} 3·274. Monoclinic; optical extinction on the clinopinacoid, 4° from the *c*-axis. Analysis gave:

ZnO.	CuO.	Fe_2O_3.	Insol.	CO_2.	H_2O.	Moisture.	MgO.	SO_3.
58·12	17·94	1·46	0·22	12·55	9·44	0·28	trace	trace

L. J. S.

Phosphorite from the Ural Mountains. V. Tschirvinsky (*Jahrb. Min.*, 1915, i, Ref. 28; from *Bull. Soc. Oural. Sci. Nat.*, 1913, **32**, 105—120).—A phosphorite vein occurs at the contact of granite and chlorite-schist near the village of Pachkun, 15 versts from the Reshevsk smelter. Near the surface, the material is earthy, but at a greater depth it is compact, and sometimes brecciated. The following analysis corresponds with $Ca_3(PO_4)_2$ 82·50, CaF_2 4·76, $CaCO_3$ 4·84%.

CaO.	Fe_2O_3.	Al_2O_3.	P_2O_5.	CO_2.	F.	Cl.	H_2O.*	Insol.	Total, less O for F.
50·59	1·84	1·86	37·79	2·13	2·32	trace	2·27	2·05	99·88

* Hygroscopic water, 0·87; water of crystallisation, 1·40; loss on ignition, 4·84%.

The vein is probably of hydrothermal contact origin, and is the first phosphorite deposit of this type met with in Russia.

L. J. S.

Monazite from Bahia, Brazil. J. Uhlig (*Centr. Min.*, 1915, 38—44).—Specimens from Bom Jesus dos Meiras, in the province of Bahia, show well-developed crystals of monazite in association with pink topaz, emerald, and magnesite. The yellowish-brown monazite crystals ($\frac{3}{4}$ cm. across) present a prismatic habit, owing to the predominance of the form $v(111)$; $a:b:c=0·9693:1:0·9154$; $\beta=76°6'$. D 5·162; hardness, 5. The following analysis, agreeing with the formula $R'''PO_4$, shows an unusually small amount of thoria and a predominance of cerium earths (Nd_2O_3, Pr_2O_3, and La_2O_3) over the ceria.

P_2O_5.	ThO_2.	Ce_2O_3.	$(Nd,Pr,La)_2O_3$.	Y_2O_3.	CaO.	Insol. in H_2SO_4.	H_2O.	Total.*
29·34	0·05	26·06	39·92	2·78	0·41	0·40	0·54	99·50

* Also traces of Fe, Mn, Mg.

Magnesite, occurring as small (1 mm.) rhombohedra intergrown with the monazite, gave analysis I; larger (1 cm.), colourless, and transparent crystals of magnesite gave II.

	CO_2.	MgO.	CaO.	FeO.	Rare earths.	P_2O_5.	Insol in HCl.	Moisture.	Total.
I.	50·27	46·09	0·28	0·67*	0·45	0·17	1·78	0·06	99·77
II.	51·9	47·4	0·7	0·5	—	—	—	—	100·5

* Partly Fe_2O_3.

L. J. S.

Meerschaum from the Agram Mountains. FRAN TUĆAN (*Centr. Min.*, 1915, 73—77).—A white mineral with a finely fibrous structure occurs as small veins in a red, weathered serpentine at the village of Orešje gornje. Under the microscope, it is seen to be completely crystalline; the fibres extinguish straight, and the sign is positive in the direction of their length. $D^{22}=2{\cdot}02$. The following analysis agrees with the formula $H_4Mg_2Si_3O_{10},2H_2O$. Over calcium chloride, the material loses 4·93% water, which is reabsorbed from a moist atmosphere. At 88°, the loss of water is 11·08%, and at 225° 13·15%.

SiO_2.	Fe_2O_3.	NiO.	MgO.	H_2O (<107°).	H_2O (>107°).	Total.
53·05	0·97	0·31	23·50	12·02	9·52	99·37

The material takes up various organic colouring matters, the fibres becoming pleochroic as seen under the microscope.

L. J. S.

Petalite from Elba. PROBO COMUCCI (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 1141—1146).—Analysis of a sample of petalite from Elba gave the following results:

SiO_2.	Al_2O_3.	Fe_2O_3.	Li_2O.	K_2O.	Total.
77·58	18·25	0·58	3·08	0·83	100·32

If the ferric oxide is calculated as alumina, these numbers agree well with the formula $14SiO_2,2Al_2O_3,Li_2O$ or $2(6SiO_2,Al_2O_3)+2SiO_2,Li_2O$, whereas ordinary petalite (from America or Sweden) has the formula $8SiO_2,Al_2O_3,Li_2O$ or $6SiO_2,Al_2O_3+2SiO_2,Li_2O$. The author is unable to confirm the supposed isomorphism of petalite and spodumene (compare Rammelsberg, "Handbuch der Mineralchemie," 1875, II., 424). T. H. P.

Mineralogical Study of Lepidolite from Elba. PROBO COMUCCI (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 1068—1073).—A sample of lepidolite from Elba, D 2·842, gave the following results on analysis:

SiO_2.	Al_2O_3.	Fe_2O_3.	TiO_2.	MnO.	K_2O.	Li_2O.	F.	H_2O.	Total, less O for F.
48·05	28·18	2·51	0·16	2·13	7·77	5·27	6·32	1·65	99·39

If the ferric oxide is calculated as alumina, the most suitable formula for the mineral is $7SiO_2,3Al_2O_3,K_2O,2Li_2O,4F,H_2O$.

T. H. P.

Vesuvianite and Hastingsite in the Nepheline-Syenite of Almunge, Sweden. PERCY QUENSEL (*Centr. Min.*, 1915, 201—208).—Prismatic crystals of vesuvianite occur as an accessory constituent in a theralitic nepheline-syenite (called canadite) in the umptekite massif of Almunge, near Upsala. Analysis I, by R. Mauzelius, gives the ratio $RO:R_2O_3=3{\cdot}3:1$, instead of the normal 4:1. Vesuvianite is typically a contact-metamorphic mineral

occurring in calcareous rocks, and its presence as an original constituent in an igneous rock is unusual.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.
I.	36·16	2·49	17·59	3·91	1·80	0·34
II.	37·49	0·86	10·81	7·53	25·14	0·95

	MgO.	CaO.	K_2O.	Na_2O.	H_2O.	Total.
I.	0·81	33·67	0·13	0·86	2·10	99·86
II.	1·34	9·77	1·91	2·06	2·01	99·86

A velvet-black amphibole with optical characters similar to those of the hastingsite from the nepheline-syenite of Hastings Co., Ontario, occurs in the umptekite of Almunge; anal. II, by R. Mauzelius. L. J. S.

The Water of Stilbite is Chemically Combined. A. Beutell and K. Blaschke (*Centr. Min.*, 1915, 4—11).—Dehydration experiments were made with the radiated stilbite from the granite of Striegau, in Silesia. Analysis of this material gave:

SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	H_2O.	Total.
56·35	16·80	7·56	0·82	0·58	17·79	99·90

corresponding with $(Ca,Na_2,K_2)O,Al_2O_3,6SiO_2,6{\cdot}4H_2O$. In sixty-three of the earlier, more trustworthy, analyses, the water varies between 5 and 7 molecules, $6H_2O$ being usually given in the text-books. Powdered stilbite in an atmosphere saturated with water-vapour at 17° absorbs water until it holds 6·95 molecules. The formula therefore becomes $CaAl_2Si_6O_{16},7H_2O$. At 17° in a vacuum, 6·77% H_2O is lost in eighty-seven hours, and over phosphoric oxide 10·92%. In a vacuum at 100° the loss is 14·72%, and at 470° the whole of the water is lost, whereas at the ordinary atmospheric pressure a red heat is needed to expel all the water. After complete dehydration, the material does not reabsorb water. Material dehydrated to the extent of 17·00% was maintained in equilibrium at various temperatures, ranging from 17° to 380°, in a current of air saturated with water-vapour, and it was found that the percentage of water remained practically constant through definite intervals of temperature, corresponding with fourteen different hydrates. The hydration curve shows a series of steps, each corresponding with $\frac{1}{2}H_2O$ in the formula as given above. The formula of stilbite is therefore written $Ca_2Al_4Si_{12}O_{32},14H_2O$. The dehydration curves (as distinct from the hydration curve now given) previously obtained by Rinne and by Friedel are continuous. This is explained by the fact that the rate at which water is lost depends on the size of the particles, and the cohesion of the material thus becomes a factor. L. J. S.

The Supposed Existence of Absorbed Water in Crystallised Hydrosilicates. A. Beutell and K. Blaschke (*Centr. Min.*, 1915, 195—200. Compare preceding abstract).—A further discussion of the dehydration and hydration curves of hydrated silicates, with

criticisms of the conclusions of Rinne, Friedel, and Zambonini. The case for the existence of dissolved or absorbed water in hydrated silicates is considered as not proved. L. J. S.

Exchange of Bases in Stilbite. A. Beutell and K. Blaschke (*Centr. Min.*, 1915, 142—144).—Powdered stilbite from Striegau, Silesia, was shaken in a solution of ammonium chloride at a constant temperature of 28°. After two and a-half days, 51% of the calcium was replaced by an equivalent amount of ammonium, and after fifteen days 96%. In an ammoniacal solution of ammonium chloride this reaction proceeds more quickly, and after fifteen days the whole of the calcium is replaced by ammonium. Ammonia does not, however, replace the hydroxyl group. With completely dehydrated stilbite there is very little action. L. J. S.

Leonhardite and Stilbite from Tiflis. N. Surgonov (*Jahrb. Min.*, 1915, i, Ref. 184; from *Festschrift V. Vernadski, Moskau*, 1914, 247—263).—Calcite veins in the Sololakskaya Mountain contain secondary (or β-) leonhardite, stilbite, and quartz. The leonhardite forms opaque, white prisms, D 2·272; analysis I corresponds with $Ca_2Al_4Si_8O_{24},7H_2O$. The small, colourless crystals of stilbite gave II, corresponding with $CaAl_2Si_6O_{16},6H_2O$.

	SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	H_2O (110°).	H_2O (>110°).	Total.
I.	51·32	23·03	11·72	0·34	trace	1·93	11·76	100·10
II.	57·80	16·10	8·11	0·73	—	3·00	14·70	100·44

L. J. S.

Analysis of Keffekilite from the Crimea. H. Kasperovitsch (*Jahrb. Min.*, 1915, i, Ref. 27; from *Festschrift V. Vernadski, Moskau*, 1914, 121—122).—Analysis of nearly homogeneous material from Baktschissarai gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	H_2O.	CO_2.	Total.
51·00	16·28	0·92	1·13	4·09	5·41	19·79	1·09	99·71

Deducting 2·4% admixed $CaCO_3$, these results correspond with the formula $5{\cdot}09SiO_2,1R_2O_3,1{\cdot}19RO,6{\cdot}63H_2O$. L. J. S.

Cordierite. E. A. Wülfing and Leopold Oppenheimer (*Jahrb. Min.*, 1915, i, Ref. 175—181; from *Sitzungsber Heidelberg. Akad. Wiss. Math.-nat. Kl.*, 1914, Abh. 10, 1—13). L. Oppenheimer (*Verh. Heidelberg. Naturh.-med. Ver.*, 1914, **13**, 257—302, and *Inaug. Diss. Heidelberg*, 1914).—Detailed optical determinations for light of wavelengths *A*—*K* were made on cordierite from eight different localities; the facial and axial pleochroism colours are also given. The following new analyses, by M. Dittrich, of some of the materials so investigated were made, with especial care in the determinations of ferrous and ferric iron and water: I, from Haddam,

Connecticut; II, Bodenmais, Bavaria; III, Tvedestrand, Norway; IV, Orijärvi, Finland.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	K_2O.	Na_2O.	H_2O (110°).	H_2O (>110°).	Total.
I.	48·17	32·53	1·21	6·63	8·86	0·50	1·39	0·10	1·12	100·51
II.	48·58	31·47	1·85	4·90	10·68	—	0·35	0·14	1·82	99·79
III.	49·18	32·28	0·08	4·05	11·25	0·44	0·21	0·27	2·04	99·80
IV.	49·47	33·18	1·15	4·53	10·80	0·04	0·17	0·04	1·16	100·54

Also trace of CaO in I. and II.; trace of Li_2O in I. and III.

Various alternative formulæ are suggested, but that of Farrington, namely, $10SiO_2,4Al_2O_3,4MgO,H_2O$, is the simplest. A selection of the physical characters (the optical constants those for sodium light) of the materials analysed are compared below. There is a general relation between these and the percentage of iron.

	Fe.	D.	$\frac{\alpha+\beta+\gamma}{3}$.	$\gamma-\alpha$.	2V.
I.	6·00	2·660	1·5576	0·0090	43°26′
II.	5·10	2·603	1·5449	0·0086	65°36′
III.	3·71	2·581	1·5397	0·0070	69°26′
IV.	4·33	2·581	1·5369	0·0076	79°54′

L. J. S.

Holmquistite, a Lithium-glaucophane from Utö, Sweden. A. Osann (*Jahrb. Min.*, 1915, i, Ref. 173—174; from *Sitzungsber. Heidelberg. Akad. Wiss. Math.-nat. Kl.*, 1913, Abh. 23, 16 pp.).—Needles, 2 cm. long and 0·2—0·3 mm. across, of a blue mineral occur in a fine-grained, dark grey granulitic rock in the Nyköping mine, on the island of Utö. These possess the same optical orientation (axial plane (010), c: $c=2—3°$, $2E=68°56'$, negative), pleochroism, and cleavage angle ($mm'=55°48'$) as glaucophane, but differ from this in containing some lithia in place of sodium. This constituent has probably been derived from the pegmatite veins, rich in various lithium minerals, which intersect the crystalline schists and their interbedded iron ores. The following analysis, by M. Dittrich and L. Hezner, corresponds with the metasilicate molecules 13·59 $(H,Li,Na,[MgF],K)_2(Al,Fe)_2Si_4O_{12}$ (glaucophane-riebeckite molecule), 9·66 $(H,Li,Na,[MgF],K)_2(Fe,Mg)_3Si_4O_{12}$ (arfvedsonite molecule), 1·22 $Mg_4Si_4O_{12}$ (anthophyllite molecule), with an excess of 1·33 SiO_2.

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.
60·45	trace	7·70	9·68	4·38	12·12

Na_2O.	K_2O.	Li_2O.	H_2O (−110°).	H_2O (110—1250°).	F.	Total, less O for F.
1·12	0·54	2·13	0·09	2·28	0·43	100·74

L. J. S.

Analytical Chemistry.

Quantitative Microanalysis. F. Emich (*Monatsh.*, 1915, **36**, 407—440).—The results of an extended investigation on various types of microbalances are given.

An improved form of the ordinary Nernst balance modified by Emich and Donau is described. The telescope in the older instrument is replaced by a Zeiss microscope. The sensitiveness is then 0·003 mg., and cannot be increased in this type of instrument, since the air currents inside the balance case have too great an influence on the zero position.

Two more sensitive models are described; these have a horizontal quartz beam, one arm of which functions as an index. A small metal case, such as that used by Steele and Grant in their vacuum balance, can thus be used. The weighings are accurate to 0·0003 mg. and 0·0001 mg. respectively. Quantitative analyses (estimations of residue) can thus be performed with 0·1—0·3 mg. or 0·03—0·05 mg. of material respectively, and the results are accurate to 0·2%. The following are typical of the estimations: water of crystallisation in gypsum, platinum in quinoline platinichloride, chromium in guanidine chromate, potassium and sodium (as sulphate) in potassium hydrogen tartrate and sodium chloride. Various applications of such highly sensitive Nernst balances to problems of physiological chemistry are suggested.

The torsion balance of Hartmann and Braun is very suitable for determinations of residue, a few milligrams of substance being used.

A new projection spring balance for demonstration purposes is described. H. W.

Apparatus for the Continuous Extraction of a Liquid by Another and Heavier Liquid. Isidor Greenwald (*J. Ind. Eng. Chem.*, 1915, **7**, 621).—The apparatus has the form of an ordinary Soxhlet, but without the siphon; the latter is replaced by a tube extending from the bottom of the cylindrical part of the apparatus to about one-half the height of the side-tube. The heavy solvent is placed in the apparatus, the liquid to be extracted then added until the solvent is forced so far up the connecting tube that it nearly flows into the side-tube, an extraction flask containing more of the solvent is attached, and the apparatus is connected with a reflux apparatus. As the condensed solvent from the latter falls through the liquid to be extracted, the solvent collecting below the liquid passes gradually up the connecting tube and flows down the side-tube into the flask. W. P. S.

Modified Pipette. Sidney Born (*J. Ind. Eng. Chem.*, 1915, **7**, 621).—A glass tap is provided on the upper stem of an ordinary pipette; the part of the stem above the tap is bent downwards and then outwards at about the level of the bulb of the pipette.

W. P. S.

The Specific Absorption of Reagents for Gas Analysis R. P. ANDERSON (*J. Ind. Eng. Chem.*, 1915, **7**, 587).—The volume of a gas which a certain reagent will absorb up to a point at which the gas is not completely removed from its mixture with other gases may be expressed in c.c. of gas per c.c. of reagent, and this value is termed the specific absorbing power, or the specific absorption, of the reagent. For instance, the specific absorption at ordinary temperature of a certain alkaline pyrogallol solution for oxygen, obtained by shaking a mixture of gases containing 21% of oxygen with the reagent for three minutes in a Hempel double pipette, was found to be 5, that is, the total amount of oxygen absorbed, up to the point at which the reagent no longer removed all of the oxygen in the time stated, was found to be five times the volume of the reagent employed. W. P. S.

Reagents for Use in Gas Analysis. I. Alkaline Pyrogallol. R. P. ANDERSON (*J. Ind. Eng. Chem.*, 1915, **7**, 587—596).—A solution containing 13·6 grams of pyrogallol and 71·5 grams of potassium hydroxide per 100 c.c. is recommended for use in absorbing oxygen from a mixture of gases. The specific absorption (see preceding abstract) of this solution for different conditions is given below; the temperature of the reagent was 20—24°, the initial volume of the gas sample was 100 c.c., and the volume of the reagent was 25 c.c. for the first pipette and 185 c.c. for the second.

In Hempel pipette for use with mercury:

Number of minutes samples were shaken	1	2	3	4	5
(*a*) For gases containing 20·9% oxygen	27	30	31	—	—
(*b*) For gases containing 90·0% oxygen	21	24	24	—	—

In Hempel double pipette for liquid reagents:

(*a*) For gases containing 20·9% oxygen	25	29	31	—	—
(*b*) For gases containing 90·0% oxygen	0	27	30	31	32

The objection to the use of potassium hydroxide purified by alcohol does not appear to be valid; sodium hydroxide cannot be substituted for potassium hydroxide in the preparation of the reagent. W. P. S.

Preparation of Normal Hydrochloric Acid. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1915, **28**, 264).—The author recommends potassium hydrogen carbonate as the standard substance in acidimetry and alkalimetry. The purest commercial salt generally contains small quantities of the normal carbonate, and consequently also of water. In order to obtain it pure and dry, it is ground to a fine powder in an agate mortar, and then put to dry over calcium chloride in a desiccator filled with carbon dioxide. After a few days, it is again powdered, and dried for some days more. The dry, pure salt thus obtained can be preserved in bottles stoppered with corks covered with tin foil. Experiments showed that it is a very satisfactory standard, comparison tests being made, using the method of Acree and Brunel (A., 1906, ii, 703).

In making standard hydrochloric acid, it is best to weigh out the exact equivalent of the potassium hydrogen carbonate, and then titrate this with the acid from which the standard solution is to be made. The volume of acid required to neutralise the salt is then run out from the same burette into a measuring flask, where it can be diluted to the required volume. Errors of burettes and pipettes are thus eliminated. T. S. P.

Apparatus for the Estimation of Sulphur in Gas. E. R. Weaver and J. D. Edwards (*J. Ind. Eng. Chem.*, 1915, **7**, 620—621).—The combustion chamber of the apparatus consists of a glass tube 360 mm. in length and 25 mm. in diameter; a porcelain burner tube passes through a stopper at the lower end of the combustion chamber, and the gas is ignited by means of a pair of platinum terminals placed above the burner, and forming a spark-gap. Air, passed previously over soda-lime, is admitted to the burner just below the gas jet, and a secondary supply of air is introduced into the lower part of the combustion chamber. The combustion gases are withdrawn from the top of the chamber and conducted through a series of absorption vessels. W. P. S.

Estimation of Sulphates in Water by Benzidine Hydrochloride. F. W. Bruckmiller (*J. Ind. Eng. Chem.*, 1915, **7**, 600—602).—The benzidine method (A., 1903, ii, 572, 691; 1907, ii, 196) was found to be trustworthy, the results obtained agreeing closely with those found by precipitation with barium chloride. W. P. S.

Estimation of Ammonia by the Boric Acid Method. Ferdinand Pilz (*Chem. Zentr.*, 1915, **i**, 1280; from *Zeitsch. landw. Vers.-Wesen. Osterr.*, 1915, **18**, 55—57).—The boric acid method described by Winkler (A., 1913, ii, 527) for the titration of ammonia is more complicated than the usual method used for the purpose (absorption of the ammonia in hydrochloric or sulphuric acid). W. P. S.

A Simple Clinical Method for the Estimation of Ammonia in Urine. A. A. Bonnema (*Chem. Zeit.*, 1915, **39**, 519).—Incomplete expulsion of ammonia from an aqueous medium by boiling with alkali, and danger of the hydrolysis of carbamide during this process, are avoided by distilling a mixture of urine (10 c.c.) and absolute alcohol free from aldehyde (30 c.c.) with about 0·5 gram of calcium oxide. Thirty c.c. are collected in 10 c.c. $N/10$-sulphuric acid, and, after dilution with water, the distillate is titrated with alkali, using *p*-nitrophenol as indicator. Estimation of ammonia present as amino-acids is obtained by difference between free ammonia as found by the above method, and total ammonia and amino-acids as found by a modification of Henriques and Sörensen's formol method, whereby the urine (1 vol.), diluted with water (3 vols.) and neutralised to phenolphthalein, is treated with formaldehyde solution (1 vol.) and again neutralised, the

amount of alkali required for this being a measure of the ammonia and amino-acid ammonia present. Previous purification of the urine with barium chloride and baryta water is not necessary.

G. F. M.

Estimation of Phosphorus in Biological Material and the Standardisation of Solutions of Molybdenum. A. E. Taylor and C. W. Miller (*J. Biol. Chem.*, 1915, **21**, 255—262).—The method, previously described by the authors (A., 1914, ii, 675) for the estimation of small quantities of phosphate by precipitation as yellow phosphomolybdate and subsequent titration, gives somewhat too high results, owing to the inclusion of molybdic oxide in the precipitate. The errors due to this source are diminished if the precipitation is carried out in the presence of nitric acid instead of sulphuric acid, originally recommended, and may be almost entirely avoided if only a slight excess of ammonium molybdate is employed. Full details of the method are given.

Raper's method (this vol., ii, 66) for the determination of small amounts of phosphate appears to be more accurate than the colorimetric method described by the authors (*loc. cit.*), but where great accuracy is of no special advantage, the latter method is to be preferred, on account of its greater rapidity. The colorimetric determination involves the use of standard solutions of molybdenum trioxide; a large number of methods for estimating the trioxide were investigated, the most satisfactory one being precipitation as lead molybdate in the manner described by Raper.

F. B.

Colorimetric Estimation of Phosphorus in Soil Extracts. C. E. Millar and F. A. Gangler (*J. Ind. Eng. Chem.*, 1915, **7**, 619).—The Veitch method as modified by Schreiner and Brown (A., 1905, ii, 117) yields trustworthy results when applied to the estimation of phosphorus in soil extracts, but the reagents used must be as pure as possible; a small correction is necessary for the slight coloration yielded by the reagents in the absence of phosphoric acid.

W. P. S.

Estimation of Arsenic in Organic Secretions and Tissues. Peter Klason (*Arkiv. Kem. Min. Geol.*, 1914, **5**, No. 9, 1—10).—The author points out that nitric acid is the only easily volatile mineral acid which is readily obtained free from arsenic; all that is necessary is to distil it gently from a tubulated retort. Oxidation of the organic matter containing arsenic is then carried out as follows, urine and sweat being the organic liquids dealt with by the author. A litre of urine, to which has been added 100 c.c. of the pure nitric acid, is evaporated to dryness on the water-bath. The residue is again evaporated with 50 c.c. of nitric acid, and then dissolved in a further 100 c.c. of acid, when more or less sodium chloride separates. The solution is poured into a separating funnel opening into a quartz glass distilling flask partly filled with small lumps of quartz or of pure felspar porce-

lain. The flask is heated in a bath of strong sulphuric acid, and when the temperature is 270°, the solution is gradually dropped on to the quartz lumps, the temperature not being allowed to fall below 250°. The sodium chloride is washed twice, each time with 25 c.c. of nitric acid, the acid then being run into the flask, as described above. When all the acid has distilled from the flask, pure nitric acid is run in if the quartz lumps appear dark from separated carbon until the carbon is completely oxidised. The contents of the flask are then dissolved in warm water containing a little nitric acid, and the solution evaporated to dryness on the water-bath. The residue, which should be snow-white, and consists chiefly of sodium chloride and ammonium nitrate, is then heated at 130° until no more acid vapours are evolved, after which it is dissolved in water and filtered.

The arsenic in the filtrate can then be estimated in the usual ways, the method used by the author depending on precipitation of the sulphide by means of thioacetic acid, solution of the sulphide, and electrolytic reduction of the solution to give arsine, and hence arsenic mirrors. If the mirror contains at least 0·01 mg. of arsenic, it is best estimated by direct weighing with a microbalance.

Investigations have shown that there is no necessary connexion between "arsenic-sickness" and the amount of arsenic in the urine or sweat. As a matter of fact, there was less arsenic in the urine from persons suffering from arsenic poisoning than in that from other persons, whether they were fed on a flesh or vegetable diet.

T. S. P.

A Rapid and Exact Process for the Estimation of Carbon in Iron and Iron Alloys. Ernst Szász (*Chem. Zeit.*, 1915, **39**, 482—484).—A simpler apparatus than that hitherto used for the combustion of iron (A., 1913, ii, 621) is described. An electric furnace replaces the original combustion apparatus, and the general arrangement of the oxygen-purifying tubes, the furnace, and the gas burette for the measurement of the carbon dioxide is described and figured in detail. The iron or steel shavings are mixed with a mixture of equal parts of copper and aluminium oxides, and with a furnace temperature of 1000—1100° combustion is complete in two minutes. The gases are then drawn over into the burette, which is charged with 10% sulphuric acid instead of mercury, as previously recommended. For ferrochrome, a higher temperature than that obtainable with an ordinary electric furnace is required, and the previously described expensive platinum apparatus is necessary.

G. F. M.

Estimation of Silver in Organic Preparations. F. Lehmann (*Arch. Pharm.*, 1915, **253**, 42—46).—The author has made a critical examination of the newer methods (1912—1914) for the estimation of silver in pharmaceutical preparations. The chief consideration is the rapid destruction of the organic matter, and the following procedure is recommended. The substance (0·2—1·0 gram,

according to the silver content) is dissolved in 10 c.c. of water, mixed with 10 c.c. of concentrated sulphuric acid, and then 2 grams (or more) of finely powdered potassium permanganate are gradually added, and the mixture is left for fifteen minutes. If the substance is free from chlorine, the mixture is then diluted with 50 c.c. of water, and ferrous sulphate is added until the solution is clear, when the silver is titrated by a thiocyanate solution. If the preparation contains chlorine, the mixture is concentrated until fumes of sulphuric acid are evolved, when the estimation is completed as above. J. C. W.

Analysis of Alkaline Earth Metals. C. REICHARD (*Pharm. Ze tr.-h.*, 1915, **56**, 329—331).—Calcium, strontium, and barium carbonates, precipitated together in the usual way, are dried and ignited over a blast-flame. A portion of the resulting oxides is shaken with water, the mixture filtered, and the clear filtrate heated to boiling; a turbidity indicates the presence of calcium, whilst strontium and barium may be present if the solution remains clear. The remainder of the oxides is then boiled for some time with water and filtered. An insoluble residue remains if calcium is present. The filtrate is evaporated to dryness, the residue converted into chlorides, and dried. If the chlorides are deliquescent, strontium is present; barium chloride remains unaltered when exposed to a moist atmosphere. In cases where the chlorides are deliquescent, the mass is extracted with alcohol; barium chloride is not dissolved. W. P. S.

Method for the Volumetric Estimation of Lead. FRANK DOUGLAS MILES (T., 1915, **107**, 988—1004).—In the method proposed the lead is precipitated as sulphate; this is converted into sulphide, and the liberated acid is titrated, its quantity being a measure of the amount of lead present. The mixture of lead sulphate and sulphuric acid (about 3 c.c.), produced by evaporation to the point at which white fumes are evolved, is cooled, diluted with 50 c.c. of water, the lead sulphate collected on a filter, and washed first with 5% sulphuric acid and then with dilute alcohol. The filter-paper, together with the precipitate, is then transferred to a flask, saturated sodium sulphide solution is added (10 c.c. for each 0·1 gram of lead), the upper part of the flask is heated with a flame, and the flask is closed with a rubber stopper. The contents are shaken, and maintained at about 50° for twenty minutes, then cooled, filtered through a paper-pulp filter, and the filter is washed with water. The filtrate is boiled for two minutes to expel hydrogen sulphide, and then titrated with $N/10$-sodium hydroxide solution, using methyl-red as indicator. When the lead sulphate is mixed with calcium sulphate or other finely-divided, insoluble matter, the washing with dilute alcohol may be omitted; the lead sulphate is converted into sulphide immediately after the washing with 5% sulphuric acid. The results thus obtained are slightly too high, owing to the amount of acid remaining in the filter-paper, but the error does not usually exceed 1 part in 250. The presence

of copper or barium does not interfere with the method, but when barium is present, the lead sulphate should be dissolved in boiling sodium hydroxide solution; after cooling, the lead sulphate is recovered by the addition of sulphuric acid. When iron is present, the lead sulphate is always contaminated with a ferric salt; the latter may be removed by dissolving the washed lead sulphate in a mixture of 15 c.c. of hydrochloric acid and 10 c.c. of water, adding 5 c.c. of sulphuric acid, and evaporating the mixture until white fumes are given off; the addition of 10 c.c. of sulphuric acid for the precipitation of the lead sulphate prevents the precipitation of basic bismuth sulphate should this metal be present. The method may be applied to the estimation of lead in ores; the results obtained agree within 0·2% with those found gravimetrically. W. P. S.

Electroanalysis of Copper without Platinum Electrodes. J. Guzmán Carrancia and J. Sanz Ulzurrum (*Anal. Fis. Quim.*, 1915, **13**, 289—293).—The use of platinum electrodes in the analysis of copper can be obviated by employing a copper cathode and an anode of steel wire. A. J. W.

Improved Method for the Detection of Cobalt by means of α-Nitroso-β-naphthol. F. W. Atack (*J. Soc. Chem. Ind.*, 1915, **34**, 641—643).—A solution of the sodium salt of α-nitroso-β-naphthol provides a more delicate reagent for cobalt than the acetic acid solution hitherto used. The reagent is prepared by boiling 0·1 gram of α-nitroso-β-naphthol with 20 c.c. of water and 1 c.c. of dilute sodium hydroxide solution, filtering, and diluting to 200 c.c. As little as one part of cobalt in a million may be detected by adding 1 c.c. of the reagent and 1 c.c. of ammonium chloride solution to the neutral or slightly alkaline solution under examination, when a claret coloration or a red precipitate, unaffected by acidifying with sulphuric acid, is produced. The test is not affected by the presence of zinc or manganese, and although large amounts of nickel interfere with the intensity of the coloration, they do not prevent the detection of cobalt. In presence of very large quantities of nickel, it is recommended to reduce the concentration by partial precipitation with dimethylglyoxime. G. F. M.

Reduction of Copper Oxide in Alcohol Vapour in Reducing Sugar Estimations and Copper Analysis. A. Wedderburn (*J. Ind. Eng. Chem.*, 1915, **7**, 610—611).—Cuprous and cupric oxides are readily reduced to metallic copper by hot alcohol vapour. The oxide is collected on an alundum crucible, washed, and ignited to destroy any traces of organic substances. While still hot, the crucible is transferred to a beaker containing a small quantity of boiling alcohol, the crucible being placed on a small tripod so that it does not touch the liquid. The beaker is covered, and the crucible and its contents left in contact with the alcohol vapour for about four minutes; the crucible is then cooled in a desiccator, and weighed. W. P. S.

Estimation of Blood-Sugar in Small Quantities of Blood. W. WOLFF (*Chem. Zentr.*, 1915, i, 1185; from *Deutsch. med. Woch.*, 1915, **41**, 6—8).—Bang's method (A., 1907, ii, 136; 1908, ii, 235; 1910, ii, 163) is to be preferred to that proposed by Kowarsky; the former method is more rapid and trustworthy, and requires only a very small quantity of the blood. W. P. S.

The Indicator in Pyroligneous Acid. J. M. JOHLIN (*J. Ind. Eng. Chem.*, 1915, **7**, 596).—When pyroligneous acid is neutralised with milk-of-lime, the end-point of the reaction is denoted by the production of a wine-red coloration. It is probable that pyroligneous acid contains volatile esters of pyrogallol, and that these, in neutral solution, give a coloration with the traces of iron salts present in ordinary milk-of-lime. If the latter is prepared from pure calcium oxide, it does not yield a coloration with pyroligneous acid, but the red coloration is obtained if traces of ferric salts are added previously. W. P. S.

Compounds Occurring in Commercial Calcium Acetate. ÅKE BERGH (*Arkiv. Kem. Min. Geol.*, 1914, **5**, No. 14, 1—15).—The author finds that Stillwell's method (A., 1904, ii, 374) for the estimation of calcium acetate gives results which agree excellently with that adopted by the Farbenfabriken vorm. Friedr. Bayer & Co., Elberfeld, in which the calcium acetate is distilled with phosphoric acid in a current of air free from carbon dioxide.

Three processes have been investigated for the estimation of acids other than acetic present in the distillate obtained by Stillwell's method, namely, oxidation with potassium permanganate, mercuric oxide, and hydrogen peroxide. The first two methods are well known, but oxidation with hydrogen peroxide has not been used before. It is shown that in the presence of platinised platinum, oxidation of formic acid takes place readily, whereas acetic, propionic, and butyric acids are not affected.

Comparison of the results obtained by the various methods with different samples of calcium acetate shows that the mercuric oxide method gives the highest results for formic acid, whilst hydrogen peroxide gives the lowest results in most cases. T. S. P.

Estimation of Hydrocyanic Acid and Benzaldehyde in Kirsch Liqueur. J. GOLSE (*J. Pharm. Chim.*, 1915, [vii], **12**, 44—56).—The French official method for the estimation of hydrocyanic acid and benzaldehyde in liqueurs is considered to be untrustworthy, owing to the fact that too small a quantity of alkali hydroxide is used to fix the hydrocyanic acid during the distillation of the benzaldehyde, and also because of the wrong conditions under which the latter constituent is precipitated and separated in the form of its phenylhydrazone. The following modification of the method is recommended. Two hundred c.c. of the liqueur are treated with 1 c.c. of sodium hydroxide solution (D 1·32—1·36), and distilled until 175 c.c. of distillate (*A*) have been collected. The contents of the distillation flask are now cooled, 50 c.c. of 10% sulphuric acid are added slowly, and the mixture is again

distilled, 50 c.c. of distillate (*B*) being collected in a receiver containing 5 c.c. of ammonia. The distillate (*A*) is treated with 5 c.c. of phenylhydrazine reagent (prepared by dissolving 1 gram of phenylhydrazine in a mixture consisting of 4 c.c. of glacial acetic acid, 2 grams of sodium acetate, and 20 c.c. of water, then adding 1 c.c. of sodium hydrogen sulphite solution, and filtering the whole mixture), diluted to 200 c.c., and 75 c.c. are distilled over and added to the distillate (*B*); the residual solution in the distillation flask is then heated on a water-bath for two hours (compare A., 1906, ii, 312), the flask being closed. After cooling, the precipitated benzaldehydephenylhydrazone is collected on a filter, washed with water, dissolved by pouring alcohol and ether on the filter, the alcohol-ether solution is evaporated, and the residue weighed; its weight multiplied by 2·7 gives mg. of benzaldehyde in 1 litre of the liqueur. The distillate (*B*) is treated with 1 c.c. of 10% potassium iodide solution, and then titrated with *N*/20-silver nitrate solution until a permanent opalescence is obtained; the number of c.c. of silver nitrate solution required, multiplied by 13·5, gives the mg. of hydrocyanic acid present per litre of liqueur. Three genuine samples of kirsch liqueur examined contained from 17·6 to 35·8 mg. of hydrocyanic acid, and from 29·7 to 37·3 mg. of benzaldehyde, per litre. W. P. S.

Action of Formaldehyde on Alcohols in Presence of Concentrated Sulphuric Acid. J. Buraczewski and W. Matejko (*Chem. Zentr.*, 1914, ii, 616; from *Österr. Chem. Zeit.*, 1914, [ii], **17**, 130—131).—Addition of formaldehyde to a mixture of concentrated sulphuric acid and ethyl alcohol causes an intense coloration, which increases on warming. After boiling, the addition of water precipitates considerable quantities of greenish-black, solid substance. In presence of much water, the coloration only appears on boiling. With higher alcohols, an intense coloration is produced with still greater readiness, and this observation has been adapted by the authors to the estimation of fusel oil in raw spirit. The addition of $\frac{1}{2}$—$\frac{1}{64}$% of fusel oil produces a distinct colour change. Perfectly pure methyl alcohol behaves in the same way as ethyl alcohol, but ordinary specimens are coloured on the addition of sulphuric acid alone, sufficient formaldehyde being already present as impurity in the alcohol. The precipitates obtained on dilution with water are coloured yellowish-brown by ammonia; they are almost insoluble in pure water, but soluble in carbon disulphide. G. F. M.

Estimation of Urea in Small Quantities of Blood. A. Hahn (*Chem. Zentr.*, 1915, i, 1230—1231; from *Deutsch. med. Woch.*, 1915, **41**, 134—136).—The urease method (this vol., ii, 599) may be simplified as follows. One c.c. of the serum is placed in a 50 c.c. flask, diluted with 20 c.c. of water, a small quantity of the dry enzyme and three drops of toluene are added, and the flask is closed with a stopper. A similar mixture, but without the enzyme, is prepared in another flask. After ten hours, the mixtures are each treated with 20 c.c. of *N*/100-hydrochloric acid, 0·5 c.c. of

5% potassium iodate solution, and a crystal of potassium iodide; 20 c.c. of $N/100$-thiosulphate solution are then added to each mixture, and the excess of thiosulphate titrated with $N/100$-iodine solution. The difference in the quantity of the iodine solution required for the two titrations, multiplied by 0·0003, gives the amount of urea in 1 c.c. of the serum. For the estimation of urea in urine, 1 c.c. of the latter is diluted in a flask with 10 c.c. of water, two drops of methyl-orange solution are added, and the solution is titrated with $N/10$-hydrochloric acid until the indicator shows an orange-yellow (not red) colour; a small quantity of the dry enzyme and three drops of toluene are then added, the flask is closed, and, after twenty-four hours, the mixture is titrated with $N/10$-hydrochloric acid. W. P. S.

Hæmatoxylin as an Indicator in the Titration of Alkaloids, and the Determination of the Alkaloid Content of Cinchona Bark. G. Frerichs and E. Mannheim (*Arch. Pharm.*, 1915, **253**, 117—135).—Many workers have found that the method described in the German Pharmacopœia for the estimation of alkaloids is unsuitable. The process consists, roughly, in dissolving the bases from the chloroform and ether extract with an excess of 0·1N-hydrochloric acid, and titrating the excess with 0·1N-potassium hydroxide until the yellow colour given by a grain of "hæmatoxylin" changes to bluish-violet. The authors have found that many of the difficulties are due to the oxidation of the dye in alkaline solution to hæmatein, which it is that gives the yellow and blue colours. Even if a solution of the dye containing hæmatein is employed as the indicator, the results are inconsistent, for the alkaloid interferes with the end-point.

The direct titration with 0·1N-hydrochloric acid is trustworthy, and is recommended in the Swiss Pharmacopœia. The alkaloid is dissolved in 10 c.c. of alcohol, mixed with three drops of 1% hæmatoxylin and 10 c.c. of water, and titrated until the blue colour changes to brownish-red, when a further 50 c.c. of water are added. The colour again becomes blue, and the acid is now run in until a sharp change to yellow takes place.

The authors also criticise the official process for the valuation of cinchona bark, and propose a much simpler modification.

J. C. W.

[Detection of Indican.] Adolf Jolles (*Montash*, 1915, **36**, 457—470).—See this vol., i, 838.

Estimation of Acid and of Alkaline Substances in Mineral Soils. A. Stutzer and W. Haupt (*J. Landw.*, 1915, **63**, 33—45).—In estimating acidity the following method, based on Baumann and Gully's qualitative test (*Naturw. Zeitsch. Land. Forstwirts*, 1908, 1) is employed. The soil, dried at 100° (40 grams), is treated with 50 c.c. each of solutions containing, respectively, 120 grams of potassium iodide per litre and 5 grams of potassium iodate per litre (prepared with water previously boiled), and shaken for fifteen minutes, after which 300 c.c. of water, which has been boiled and

cooled to 17—20°, are added. After being well shaken, the liquid is filtered through asbestos (not filter-paper, which absorbs some of the iodine), rejecting the first 50 c.c., and titrated with 0·01*N*-thiosulphate solution, after adding freshly prepared, thin starch solution. One c.c. of thiosulphate solution = 0·00001 gram of hydrogen, or 0·00049 gram H_2SO_4.

Soils containing particles of calcium carbonate may contain acid silicates, organic acids, and acid colloids, so that roots of plants are in contact with acids. One soil, containing more than 1% of calcium carbonate, contained 0·014% of acid.

In estimating alkalinity, the soil (40 grams) is treated with 400 c.c. of water, previously boiled and cooled to 17—20°, shaken for thirty minutes, and filtered through a large double filter. To 300 c.c. of clear filtrate, thin starch solution is added, and then 25 c.c. of the potassium iodide and iodate solutions. It is then treated with 25 c.c. of 0·01*N*-sulphuric acid, and titrated with 0·01*N*-thiosulphate until the blue colour disappears.

N. H. J. M.

Analysis of Soils containing Pyrites. V. Rodt (*Chem. Zentr.*, 1915, i, 1224—1225; from *Gesundheitsingenieur*, 1915, **38**, 10).—The following procedure is recommended: 100 grams of the soil are extracted with boiling water, and the iron (*A*) is estimated in the aqueous solution. Another portion of 100 grams of the soil is digested for thirty minutes on a water-bath with hot, dilute hydrochloric acid (1 : 3), then boiled for a short time, and the mixture is filtered; the filtrate is evaporated with the addition of chloric acid, and the sulphuric acid (*B*) estimated in the residue obtained. The portion of the soil insoluble in dilute hydrochloric acid is then rinsed into a beaker with dilute nitric acid (1 : 3), bromine water is added, the mixture heated on a water-bath, filtered, and the filtrate divided into two equal portions. One of these portions is evaporated to dryness with the addition of nitric acid, the residue is treated with concentrated hydrochloric acid, the solution filtered, and the iron precipitated as ferric hydroxide; the latter is collected, washed, dissolved in hydrochloric acid, the solution evaporated, and the quantity of iron (*C*) estimated iodometrically. The other portion of the filtrate is treated with hydrochloric acid and chloric acid, evaporated, and the sulphuric acid (*D*) estimated by precipitation as barium sulphate. For the estimation of free sulphur (*E*), 100 grams of the soil are extracted with hydrochloric acid, the insoluble portion is separated and dried over sulphuric acid under reduced pressure, and then extracted with carbon disulphide; after the solvent has been removed from the extract, the residue is treated with magnesium oxide and a small quantity of dilute nitric acid, then oxidised by heating with concentrated nitric acid, and the resulting sulphuric acid precipitated, and weighed as barium sulphate. The amount of pyrites in the sample is calculated from the quantity of iron (*C*) and that of the sulphur (*D*) after the latter value has been corrected for the quantity of free sulphur present.

W. P. S.

General and Physical Chemistry.

A Spectrum Associated with Carbon in Relation to the Wolf-Rayet Stars. THOMAS R. MERTON (*Proc. Roy. Soc.*, 1915, [*A*], **91**, 498—503).—By passing heavy condensed discharges through vacuum tubes containing hydrogen at moderately low pressure, and provided with graphite or carbon electrodes, a spectrum is obtained the lines of which are apparently coincident with some of the most conspicuous lines in the spectra of the Wolf-Rayet stars. It is not claimed that the identity of the spectra has been completely established, but the results warrant the suggestion that the origin of the Wolf-Rayet lines in question is the same as that of the vacuum-tube spectrum which is described by the author. H. M. D.

Ionisation Potentials of Mercury, Cadmium and Zinc, and the Single- and Many-lined Spectra of these Elements. J. C. MCLENNAN and J. P. HENDERSON (*Proc. Roy. Soc.*, 1915, [*A*], **91**, 485—491).—According to Franck and Hertz (A., 1914, ii, 515), the ionising potential of mercury vapour is 4·9 volts. When the heated vapour is traversed by electrons the energy of which is somewhat greater than this limiting value, it is found that the single-line spectrum λ 2536·72 is emitted. According to the quantum theory, the above potential corresponds almost exactly with the frequency of this spectral line.

The authors find that the vapours of cadmium and zinc can also be stimulated to the emission of single-line spectra when traversed by electrons possessing the requisite amount of energy. The wavelength of the cadmium line is λ 3260·17, and that of the zinc line λ 3075·99. The minimum ionisation potentials, calculated from the corresponding frequencies by application of the quantum theory, are 3·74 and 3·96 volts respectively.

No attempt has been made to determine these minimum potentials experimentally, but it has been found that the single-line spectra are not obtained if the arcing potential exceeds 12·5 volts for mercury, 11·85 volts for zinc, and 15·3 volts for cadmium. If these values are exceeded, the many-lined spectra are obtained.

It is supposed that the minimum ionisation potentials (4·9, 3·96, and 3·74) represent the amounts which are required to remove a single electron from the atoms of mercury, zinc, and cadmium respectively, and that the minima corresponding with the emission of the many-lined spectra afford a measure of the energy required to remove the outer ring of electrons from the atoms of the three elements. It would seem possible to correlate the different spectra with disturbances in definite portions of the atom. H. M. D.

Comparison of the Arc and Spark Spectra of Nickel produced under Pressure; with a Note on the Influence of Temperature and Density Gradients on the Displacements of Spectrum Lines. W. GEOFFREY DUFFIELD (*Phil. Mag.*, 1915, [vi], **30**, 385—394).—The results obtained in the author's investigation of the influence of pressure on the arc spectrum of nickel (this vol., ii, 298) are compared with those obtained by Bilham (A., 1914, ii, 786), who examined the effect of pressure on the spark spectrum of the metal. Accepting the classification of the lines given by Bilham, the comparison shows (*a*) that the displacements per atmosphere of reversed lines are smaller for the spark than for the arc spectrum; (*b*) that for unreversed lines the displacements per atmosphere are appreciably the same for the two types of spectrum. The pressure range involved in the comparison is limited to 1—10 atmospheres.

The author inclines to the view that the differences between the arc and spark displacements are due to the differences in the positions of the absorption lines upon bright lines the displacements of which are nearly, if not exactly, the same, whether produced in the arc or spark discharge. The difference in the displacements of the reversed parts of lines in the two spectra is due to the fact that the density and temperature gradients are different in the two types of discharge. H. M. D.

The High-frequency Spectrum of Tungsten. JAMES BARNES (*Phil. Mag.*, 1915, [vi], **30**, 368—370).—Photographs of the spectrum of the *X*-rays coming from a Coolidge tube with a tungsten anticathode show that the "*L*" series contains lines of wave-length $\lambda 10^8 = 1{\cdot}477$, $1{\cdot}312$, $1{\cdot}296$, $1{\cdot}277$, $1{\cdot}258$, $1{\cdot}113$, and $1{\cdot}082$ cm. The first line corresponds with the α-line referred to by Moseley (A., 1914, ii, 326). $\lambda 1{\cdot}296$ and $\lambda 1{\cdot}258$ fill exactly the gaps in the curves plotted from the β- and γ-lines of the *L* series for the elements from zirconium to gold. $\lambda 1{\cdot}277$ is supposed to represent the ϕ-radiation. For the remaining three lines there are as yet no analogues in the spectra of other elements.

According to the relation $\nu = C(N-1)^2$, where ν is the frequency, *C* a constant, and *N* the atomic number, the wave-length of the α-line of the "*K*" series should be $\lambda 10^8 = 0{\cdot}22$. The photographs show no signs of this line, but there is evidence of a more or less continuous spectrum in this region. H. M. D.

The Rotatory Dispersion of Potassium Irido-oxalate. GEORGES BRUHAT (*Bull. Soc. chim.*, 1915, [iv], **17**, 223—227. Compare this vol., ii, 302).—Solutions of active potassium irido-oxalates exhibit the phenomena of abnormal rotatory dispersion and circular dichroism. The author has measured the ellipticity and rotation produced by a 2% solution of potassium *d*-irido-oxalate, $K_3Ir(C_2O_4)_3,2H_2O$, between $\lambda = 695\,\mu\mu$ and $439\,\mu\mu$. The rotatory dispersion is considerable in the yellow and green portions of the spectrum, the rotation reaching a maximum, $[\alpha] = 300°$ at $\lambda = 495\,\mu\mu$, at the commencement of the absorption band, and

becoming zero in the violet in the interior of this band at $\lambda = 455\ \mu\mu$. The dichroism, which is zero in the red, increases slowly, and reaches a maximum in the violet at about the same wave-length, where the rotation is zero. These results confirm the generality of the phenomena of abnormal rotatory dispersion and circular dichroism in the neighbourhood of absorption bands, and also show the complete analogy of the dissymmetry of structure of an active medium arising from the presence of an asymmetric carbon atom or of an asymmetric iridium atom. W. G.

Fluorescence and Resonance of Sodium Vapour. II. (Hon.) R. J. Strutt (*Proc. Roy. Soc.*, 1915, [*A*], **91**, 511—523. Compare this vol., ii, 399).—Further experiments relating to the phenomena of resonance radiation in sodium are described. It has already been shown that the *D*-line, when allowed to fall on sodium vapour, gives rise to a lateral re-emission of light of the same wave-length. Whether stimulation of the vapour by a higher member of the principal series would give rise to the emission of the *D*-line (the first member of the series) is the particular question which has been investigated in this paper.

The experimental work has been facilitated by the use of a quartz sodium arc lamp, which gives a brilliant sodium spectrum. By the use of this lamp, it was found that eight lines of the principal series were obtained with half an hour's exposure on a small quartz spectrograph. The resonance radiation due to the *D*-line is also shown incomparably better than with any form of salted flame. The advantage lies, not only in the brilliancy, but also in the narrowness of the line.

The results obtained show that the stimulation of sodium vapour by the second member of the principal series of lines (λ 3303) gives rise to the lateral emission of the *D*-line. Ultra-violet light does not, in general, produce this effect, which may therefore be definitely ascribed to the sodium line. Stimulation by λ 3303 does not give rise to any observable resonance radiation of the same wave-length nor to any emission of the subordinate series lines.

By the use of the zinc arc, it has been found possible to stimulate sodium vapour by the less refrangible component of the doublet which λ 3303 represents. In these circumstances, not one only, but both of the *D*-lines, are emitted in about equal intensity. This result is remarkable in that Wood and Dunoyer (*Phil. Mag.*, 1914, [vi], **27**, 1018) found that stimulation by D_2 was unable to excite D_1. H. M. D.

The Natural Optical Activity of Liquids and Gases. M. Born (*Physikal. Zeitsch.*, 1915, **16**, 251—258).—A theoretical paper in which the question of the possibility of explaining the optical activity of liquid and gaseous substances on the assumption that the molecule contains asymmetrically combined electrons is subjected to rigorous mathematical analysis. The conclusions to which this leads are that a molecule which contains only three particles cannot be optically active, but that every molecule which consists

of more than three may be optically active if its structure is sufficiently asymmetrical. The simplest structure is that represented by an asymmetric tetrahedron. Any particle which is not mechanically coupled with the others contributes nothing to the optical activity. H. M. D.

The Rotatory Dispersive Power of Organic Compounds. VI. Complex Rotatory Dispersion in Ethyl Tartrate. THOMAS MARTIN LOWRY and THOMAS WILLIAM DICKSON (T., 1915, **107**, 1173—1187; see T., 1913, **103**, 1067; 1914, **105**, 94).—Methods of distinguishing between simple, complex, and anomalous rotatory dispersion are described. The rotatory power of ethyl tartrate at different temperatures and in several solvents has been examined, and found to be complex in all cases. It was found on fractionating several specimens of the ester that the lower rotation observed in the first fractions was more pronounced for violet light than for the other colours used, these variations of rotatory power not being dependent on the presence of inactive or racemic ester. Attempts were made, by cooling the heated ester suddenly or by quick solution in formamide or in ethylene bromide, to detect a thermal lag or mutarotation, similar to that observed in nitrocamphor. The results were wholly negative, but are not regarded as disproving the assumption that mutarotation occurs, this change, it is suggested, being probably so rapid as to elude the means of observation. The rotation of ethyl tartrate has been observed both visually and photographically for light of a large number of wave-lengths—from Li 6708 to Fe 3879—and in twenty-eight different solvents. The data obtained are shown as dispersion-rotation curves, and in several instances are represented by Drude expressions containing two terms in which the rotation constants are opposite in sign, whilst the term with the greater rotation constant has the smaller dispersion constant. The peculiarities of these curves are discussed. T. S. PA.

The Rotatory Dispersive Power of Organic Compounds. VII. Complex Rotatory Dispersion in Methyl Tartrate. THOMAS MARTIN LOWRY and HAROLD HELLING ABRAM (T., 1915, **107**, 1187—1195).—Ethyl tartrate being difficult to prepare in a pure condition (see preceding abstract), similar experiments to those carried out with that ester have been repeated on methyl tartrate, which, on account of its crystalline condition, can be obtained in a really pure state. No mutarotation could be observed in this case either, although the ester exists in two modifications, of m. p. 48° and 61·5° respectively. Tables are given showing the specific rotation of the ester at 20° and at 100·5°, as well as in solution in ethylene chloride, in formamide, in acetone, in water, in pyridine, and in quinoline for light of some twenty-three wave-lengths from Li 6708 to Fe 3750. The results are shown as dispersion-rotation curves, the peculiarities of which are discussed, the curves being shown to agree closely with mathematical expressions of the Drude type containing two terms. The investigation shows that the com-

plex dispersion of methyl tartrate may be expressed as the sum of two simple dispersions, and this is considered to be in agreement with the idea of Biot and Arndtsen, that anomalous rotatory dispersion is caused by the co-existence of two modifications of the active substance, these modifications changing so quickly that no mutarotation can be observed. Conversely, anomalous rotatory dispersion may prove to be a valuable indication of dynamic isomerism and other facile changes of structure. T. S. Pa.

The Rotatory Dispersive Power of Organic Compounds. VIII. An Exact Definition of Normal and Anomalous Rotatory Dispersion. Thomas Martin Lowry (T., 1915, **107**, 1195—1202).—It is found that the rotation-dispersion data for many substances may be represented by the simplest Drude equation, $\alpha/(\lambda^2-\lambda_0^2)=$ const., whilst all cases of complex dispersion which have been studied can be expressed by an equation containing two such terms. The anomalous character of a dispersion curve is shown by the existence either of a point of inflexion, a maximum, a reversal of sign of rotation, or by all three together, the conditions for these being defined. A simple dispersion-rotation curve is a rectangular hyperbola; complex dispersion is indicated when all the terms of the Drude expression are of the same sign, the curves then being somewhat similar in appearance to a rectangular hyperbola lying wholly in the angle between the asymptotes, and running smoothly without any reversal of curvature from the horizontal to the vertical asymptote. This type of curve may be described as normal, but complex. When the terms of the Drude expression are of opposite sign, the dispersion is complex; if the curve lies wholly on one side of the wave-length axis it may again be classed as normal, but if it cross the axis so as to involve a reversal of sign, the dispersion must be classed as anomalous. The dispersion-rotation curves of the two preceding papers are discussed in regard to these definitions. Some of the curves are normal, some are anomalous, but none is found to be simple. None of the experimental curves shows all three anomalies simultaneously, and therefore a complete family of curves has been calculated from a two-term formula to exhibit the various possible characteristics. The variation in the form of the curve from simple negative dispersion through complex normal dispersion, and complex anomalous dispersion to simple positive dispersion, is thus shown. T. S. Pa.

The Mechanism of Mutarotation in Aqueous Solution. James Colquhoun Irvine and Ettie Stewart Steele (T., 1915, **107**, 1230—1240).—Böeseken, from results obtained by his conductivity method, has allocated definite configurations to α- and β-glucose. The authors consider it, however, not absolutely certain that the hydroxyl groups 5 and 6 are opposed, or that they are arranged in the same manner in both substances. Böeseken regards his results as against the view that the change from α- to β-glucose involves the intermediate formation of an aldehydic or aldehydrol form. Further considerations affecting these views are now

advanced. The mechanism of mutarotation in aqueous solution will depend on (*a*) whether or not water is added to the sugar during the change, and (*b*) whether the new hydroxyl group thus introduced is attached to the terminal carbon atom of the chain or to the oxygen atom of the ring. The conductivity method has been applied to this question. Tetramethyl-α-methylglucoside, which contains no hydroxyl group, was first examined, and showed a behaviour suggesting the existence of one hydroxyl group in the molecule. This is presumably added on at the oxidic ring (see T., 1906, **89**, 1578), but no indication of this is given in the specific rotation of the substance in boric acid solution as contrasted with that in water. The conductivity of tetramethylglucose in *N*/2-boric acid solution shows first a depression, followed by a rapid rise to a considerable maximum exaltation, and then a slight fall. Three similar stages were observed in the mutarotation of this substance. It is therefore concluded that tetramethyl-α-glucose exists, in the first place, as the monohydric alcohol,

$$OMe\cdot CH_2\cdot CH(OMe)\cdot CH\cdot[CH\cdot OMe]_2\cdot CH\cdot OH,$$

and from analogy to tetramethyl-α-methylglucoside it may be concluded that in aqueous solution the sugar does not assume the aldehydic form, but that of an oxonium hydrate, from which, by abstraction of water, there may arise either the α- or the β-form of the sugar (E. F. Armstrong, T., 1903, **83**, 1305), both of which, from the conductivity evidence, ultimately exist in solution as oxonium hydrates. The mechanism of this change is discussed. It is considered probable that the mechanism of mutarotation varies with the solvent employed. T. S. P.

Phototropy in Solutions. I. B. Foresti (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 270—276).—The only compound known to exhibit phototropism in solution is di-9-hydroxyphenanthryl-10-amine (compare Schmidt and Lumpp, A., 1909, i, 34). The reddening of solutions of benzaldehydephenylhydrazone in alcohol and in alcohol acidified with acetic acid has been shown by Stobbe and Nowak (A., 1913, i, 1200) to be due, not to a transposition of the hydrazone (compare Baly and Tuck, T., 1906, **89**, 988), but to oxidation under the catalytic influence of light. The author finds that a similar oxidation takes place more rapidly in benzene solutions of benzaldehydephenylhydrazone, the red coloration thus produced disappearing in the dark. This action takes place only in presence of a very small proportion of air, and it may be repeated many times; either entire lack or excess of oxygen results in the disappearance of the phototropic properties of the solution. Since this phenomenon is not exhibited by the freshly prepared compound, but is observed only after the action of a limited amount of oxygen for some time, it appears that the phototropy belongs, not to the phenylhydrazone itself, but to some derivative of unknown constitution. The spontaneous change which benzaldehydephenylhydrazone undergoes, liberates the aldehyde, which is known to exert a marked influence on various autoxidations, and in the

present instance it is found that traces of benzaldehyde and oxygen determine the exhibition of phototropy by the freshly prepared phenylhydrazone. In toluene or xylene solution, similar phenomena are observed.

In opposition to the views of Padoa and Minganti (A., 1914, ii, 191), the author regards the action of light as a polymerisation, and that proceeding in the dark as a depolymerisation. With a benzene solution of benzaldehydephenylhydrazone, the action of sunlight displaces the limit of absorption from 550 to 510 $\mu\mu$, the solution being rendered permeable to more than one-half of the green. The maximal light action occurs between 568 and 502 $\mu\mu$.

When the temperature is raised by 10°, the velocity of decolorisation in the dark is increased in the proportion 1 : 1·6, but the velocity of coloration in the light is independent of the temperature (compare Padoa and Tabellini, A., 1912, ii, 879; Skrabal and Weberitsch, A., 1914, ii, 187). T. H. P.

The β-Rays of Radium-*D* and the Law of Absorption of β-Rays. Lise Meitner (*Physikal. Zeitsch.*, 1915, **16**, 272—276).—By means of photographs of the magnetic spectrum, it has been shown in a previous paper (Baeyer, Hahn and Meitner, A., 1911, ii, 567) that the β-rays emitted by radium-*D* consist of two groups of very low penetrating power, the velocities of which are respectively equal to 0·39 and 0·37 of the velocity of light. These results have now been confirmed by electroscopic observations. They represent the most slowly moving β-rays which have up to now been detected by means of the electroscope. The coefficient of absorption of the rays in aluminium was found to be approximately 5500 cm.$^{-1}$.

On passing through a layer of aluminium, 0·0039 mm. thick, it is found that these slowly moving rays are reduced in intensity to 10% of the original value. The velocity of the emergent rays is, however, only about 10% less than the mean velocity of the incident beam. This observation leads to the conclusion that the absorption of the rays is not due to a gradual reduction in the velocity as a result of successive collisions with a number of molecules, but that the β-particles penetrate into the interior of the absorbing atoms and are absorbed in consequence of a single collision taking place in favourable circumstances. H. M. D.

The Chemical Action of Penetrating Radium Rays. A. Kailan (*Monatsh.*, 1914, **35**, 859—887).—Ethyl acetate is decomposed by the action of the penetrating rays of radium, both when practically pure and when mixed with alcohol and water. The velocity of formation of acid under the action of the rays was measured under various conditions. In three tests, the first, in which 32·2 mg. of radium (element) was used, the second, a "blank" test in the same room where the radium was kept, both at 10° to 14°, and the third, a "blank" test in a room away from radioactive preparations, at 25°, the rate of formation of acid was four times as great in the second as it was in the third, and eight and a-half times as great in the first as in the second. In the second test, the

increased rate is ascribed to γ-rays. The primary action of the rays is regarded as a decomposition of the ester molecule with formation of acid and an unsaturated hydrocarbon. The velocity of ester formation in acetic acid and alcohol is hardly measurably increased by the action of radium rays. Acetone exposed to radium rays forms acetic acid, as in ultra-violet light, but of the order of a thousand times more slowly. F. S.

Action of Cathode Rays on Bismuth. W. P. JORISSEN and J. A. VOLLGRAFF (*Chem. Weekblad*, 1915, **12**, 741—744).—Bismuth has been proved by the spectroscopic method to contain traces of thallium, and the amount of thallium appears to be perceptibly increased by exposure of the metal to cathode rays. A. J. W.

Residual Ionisation in Gases. J. C. MCLENNAN and C. L. TRELEAVEN (*Phil. Mag.*, 1915, [vi], **30**, 415—427).—The ionisation in air which is confined in air-tight, clean zinc vessels has been found to correspond with the production of 8 to 9 ions per c.c. per second when the observations are made on land where the soil contains only such traces of radioactive substances as are found in ordinary clays and loams. On the surface of large masses of water the ionisation falls to about 4 ions per c.c. per second. This residual conductivity is found to persist when all known external radiations are cut off from the vessel containing the air, and it may be supposed that this residual ionisation is due to either (1) an extremely penetrating radiation on the earth's surface, (2) ionisation arising from the thermal agitation of the molecules, (3) spontaneous ionisation associated with exploding atoms or molecules, or (4) radiation from the walls of the containing vessel. The first hypothesis is ruled out by the observation that the ionisation has practically the same value when the containing vessel is immersed to a depth of several metres in the water of Lake Ontario (McLennan and McLeod, *Phil. Mag.*, 1913, [vi], **26**, 749). The fact that change of temperature has no appreciable influence on the residual ionisation eliminates the second hypothesis. With a view of testing the two remaining hypotheses, experiments have been made on the residual conductivity of a number of gases.

From these experiments, which were made on the ice on Lake Ontario, it seems to be established that the ionisation in air, carbon dioxide, hydrogen, nitrous oxide, and ethylene is entirely due to rays emitted by the zinc walls of the electrometer. These consist of rays of the α- and β-, and possibly of the γ-, type. On the other hand, the high residual ionisation in acetylene (27 ions per c.c. per second) cannot be entirely attributed to radiation of this kind. To a considerable extent, it must be due either to molecular collisions or to spontaneous disruption of the atoms or molecules. H. M. D.

Electrical Effects Accompanying the Decomposition of Organic Compounds. II. Ionisation of the Gases produced during Fermentation. M. C. POTTER (*Proc. Roy. Soc.*, 1915, [*A*], **91**, 465—480).—The carbon dioxide liberated by the

action of yeast on dextrose is found to contain both positive and negative ions. It is suggested that the ions present in the atmosphere may be in part due to the liberation of ionised gases from soil and water as the result of putrefactive processes. Such processes may, in consequence, exercise an important influence on natural electrical phenomena. H. M. D.

The New Element, Brevium. O. H. Göhring (*Jahrb. Min.*, 1915, ii, *Ref.* 15; from *Diss. Techn. Hochschule Karlsruhe*, 1914. Compare *Ann. Rep.*, 1913, **10**, 266).—Uranium-*X* consists of two elements, uranium-X_1 and uranium-X_2, with half-periods of 24·6 days and 1·15 minutes respectively. The latter is called *brevium*, and finds a place in the fifth group of the last line of the periodic system, being a near analogue of tantalum. The transformation scheme of the uranium series is:

$$U_1 \xrightarrow{\alpha} UX_1 \xrightarrow{\beta} UX_2 \xrightarrow{\beta} U_2 \xrightarrow{\alpha} Io \xrightarrow{\alpha} Ra.$$

L. J. S.

The Life Period of Thorium. Bertha Heimann (*Monatsh.*, 1914, **35**, 1533—1536).—The ionisation current from films of thorium oxide, known to be in equilibrium with its products, was determined, and it was calculated that, in absence of absorption, 1 milligram gives rise to 0·775 *E.S.U.* From this it was deduced that $1·99 \times 10^4$ α-particles are expelled per gram of thorium (element) per second, corresponding with the disintegration of $3·32 \times 10^3$ atoms of thorium per gram per second. This gives for the period of half-change $1·77 \times 10^{10}$ years, for the period of average life $2·56 \times 10^{10}$ years, and for λ, the radioactive constant, $3·91 \times 10^{-11}$(year)$^{-1}$. Correction must be made for lack of complete saturation of the ionisation current, and the most probable period of half-change is $1·5 \times 10^{10}$ years. F. S.

Recovery of Actinium and Ionium from the Olary Ores. S. Radcliff (*J. Roy. Soc. New South Wales*, 1914, **48**, 408—411. Compare A., 1914, ii, 237).—An actinium preparation has been obtained from the uranium concentrates derived from the ore complex occurring at Olary, South Australia. The actiniferous earths were found in the mixture of impure sulphates of lead, barium, and radium recovered in the radium extraction. Ten thousand kilos. of concentrates yield about 40 kilos. of these sulphates. Fusion with sodium hydroxide and extraction with water removed most of the lead. The residue was digested with sodium carbonate under 90 lbs. steam pressure, and, after washing, was treated with dilute hydrochloric acid. After removal of the silica by evaporating to dryness and extracting with water, the barium and radium were quantitatively precipitated by saturating the solution with hydrogen chloride. The filtrate contained the actiniferous rare earths, and was reserved for further treatment for the separation of the actinium. An ionium preparation of considerable activity

was obtained along with the thorium, from which it appears to be chemically inseparable. G. F. M.

The Extraction and Separation of the Radioactive Constituents of Carnotite. H. M. PLUM (*J. Amer. Chem. Soc.*, 1915, **37**, 1797—1816).—An account is given of an investigation of a Colorado carnotite, especially with regard to the extraction of the radioactive constituents. Carnotites are at present the most important uranium minerals, and therefore must be regarded as the chief source of radium. They vary considerably in composition, however, and therefore the methods of extraction which are usual for uranium and vanadium minerals, and which are reviewed in this paper, must be modified to suit the particular sample.

The material examined in this case was a concentrate containing about 4·27% of uranium, 5·5% of vanadium, 4% of iron, traces of barium and lead, and practically no rare earths. The mineral was not a pure carnotite, but a mixture with a vanadiferous silicate, which rendered the extraction of vanadium difficult. The total α-activity was calculated from the percentage of uranium by the method of McCoy (A., 1906, ii, 142), and the distribution of this activity was calculated from the ranges of the radioactive elements (McCoy, A., 1913, ii, 274). The determination of the activity due to actinium was based on Boltwood's work (A., 1908, ii, 454). These figures were used to find the degree of the extraction of the various active constituents.

The method of treatment which proved successful was as follows. One kilogram of the concentrates was boiled for several hours with sodium carbonate solution (400 grams of Na_2CO_3 to 2 litres). The filtrate was concentrated until crystals began to form, when 88% of the uranium separated on cooling as uranyl sodium carbonate, $UO_2CO_3,2Na_2CO_3$, which was free from radium, etc. The mother liquor was further concentrated, and the excess of sodium carbonate recovered, whilst the residual solution of sodium vanadate was found to be inactive. A second treatment of the insoluble residue with sodium carbonate was unprofitable. It was therefore boiled for eight hours with dilute hydrochloric acid, when the filtrate was concentrated and examined for the radioactive elements. Bismuth nitrate was added, and the bismuth and lead sulphides obtained by the action of hydrogen sulphide were submitted to the usual separation. The lead sulphate (0·49 gram) contained the radio-lead, whilst the polonium, deposited on copper from the bismuth chloride solution, amounted to about 50% of that present in the original ore. The filtrate from the sulphides was treated with sulphuric acid, giving 7·36 grams of barium radium sulphate, and the filtrate from this was fractionally precipitated by barium chloride in order to recover actinium. The extraction with hydrochloric acid alone did not remove the radium completely. The residue was therefore boiled for a day with dilute nitric acid. The extract contained no polonium, but yielded 0·453 gram of barium radium sulphate. By comparison with the original ore, by the emanation method, after fusion with

potassium hydrogen sulphate, it was found that 89·9% of the radium had been recovered in the barium radium sulphate. The residue, after the nitric acid treatment, was heated with 50% sulphuric acid until most of the acid had volatilised. The resulting mass was digested with water, the acid was just neutralised by ammonia, about 10 grams of cerium nitrate were added, and, finally, the solution was saturated with oxalic acid. About 61% of the ionium was precipitated with the cerium oxalate. The residue after all these extractions was white, amounted to 50·7%, and contained about 4·2% of the radium. The barium sulphate precipitates, mentioned above, were fused, converted into barium chloride, and the actinium was precipitated in the presence of aluminium hydroxide from a solution of the latter and aluminium nitrate. About 52% of the actinium was recovered.

J. C. W.

The Deposition of the Induced Radioactivity of Radium. A. DEBIERNE (*Ann. Physique*, 1915, [ix], **4**, 27—61).—For the most part a theoretical discussion of work already published on this subject (compare Mme. Curie, A., 1907, ii, 728; Wertenstein, A., 1909, ii, 713; 1910, ii, 476; 1912, ii, 887; 1914, ii, 514). The author has determined the activity induced on vertical metallic plates at different distances apart when placed in dry radium emanation and air at the atmospheric pressure for twenty-four or forty-eight hours. The activity increases with the distance between the plates, and is roughly proportional to it up to a distance of 25 mm., when it becomes practically constant. The concentration of the emanation has a very considerable effect on this distance, at which the limit is practically reached. There is only a very slight difference between the curves of activity produced by long and short activation, the limiting distance being somewhat shorter when the period of activation is shorter. Thus the deposited induced activity is mainly in the form of radium-*A*, and only a negligible quantity of radium-*B* and radium-*C*. W. G.

The Influence of Some Polyhydroxy-substances on the Electrical Conductivity of Boric Acid. J. BÖESEKEN (*Rec. trav. chim.*, 1915, **34**, 272—278. Compare this vol., ii, 136).—[With J. D. RUYS.]—Measurements were made of the conductivity of boric acid solutions containing varying molecular proportions of 1:2-dihydroxynaphthalene, 3:4-dihydroxybenzoic acid, and 3:4:5-trihydroxybenzoic acid. In every case the effect was to increase the conductivity, the increase being of the same order as that produced by catechol and pyrogallol. The carboxyl group, placed either in the meta- or para-position to the hydroxyl groups, does not appear to exert any important influence.

[With K. BRACKMANN.]—4-Nitroresorcinol has a very small conductivity, showing that the positive influence of the nitro-group on the acidity of the phenolic group disappears when two hydroxyl groups are situated simultaneously in the ortho- and para-positions to it. The conductivity of the boric acid is diminished by this

substance, and also by 3:5-dinitrocatechol. The contrast between catechol and resorcinol as to their influences on the conductivity of boric acid is not changed in principle by the introduction of the nitro-group, but is accentuated. 1:2:4-Trihydroxybenzene depresses the electrical conductivity of boric acid. W. G.

The Influence of Some Polyphenols on the Electrical Conductivity of Phosphoric Acid. J. Böeseken and K. Brackmann (*Rec. trav. Chim.*, 1915, **34**, 279—282).—An examination of the influence of certain hydroxy-derivatives of benzene on the electrical conductivity of phosphoric acid in aqueous solution shows that the effects are different to those on boric acid (compare preceding abstract). Thus catechol, pyrogallol, resorcinol, and quinol all diminish the conductivity of phosphoric acid, and practically to the same extent. W. G.

[Electrical] Conductivity of Mixtures of Solid Salts. C. Sandonnini (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 842—849).—The author has measured at various temperatures the conductivities, in the solid state, of the three mixtures previously examined in the fused state (this vol., ii, 406). The mixtures were prepared by fusion in nitrogen, in which also they were subsequently heated during the measurements.

The system $PbCl_2$–$PbBr_2$ was investigated at 200°, 250°, and 300°, all the conductivity isotherms showing a minimum corresponding approximately with the equimolecular mixture. With AgCl–AgBr, examined at 200°, 250°, 300°, 350°, and 400°, the conductivities of mixtures containing between 0 and 70 mol. % of the bromide are less, and those of the remaining mixtures slightly greater, than the values calculated by the law of mixtures; thus, the isotherms, especially for the lower temperatures, show a sharp increase in conductivity at 30 mol. % AgCl, which corresponds with the minimal temperature of crystallisation. With AgCl–TlCl, the isotherm for 200° passes through a maximum at the concentration of the eutectic mixture; other temperatures were not employed, since the eutectic mixture, containing 40 mol. % TlCl, melts at 210°, and the conductivities at temperatures below 200° are too small to give trustworthy results with the method used.

Comparison of the conductivity isotherms of the solid and fused mixtures with the solidification diagrams leads to the following conclusions. When the solidified mixtures of salts are constituted of solid solutions which may be regarded as perfectly homogeneous, and their solidification temperatures, as with $PbBr_2$–$PbCl_2$, are intermediate to those of the components, the conductivities are inferior to those calculated additively, just as is the case with dissolved or fused mixed salts containing a common ion. When, however, the components form mechanical mixtures and no other phenomenon intervenes, the conductivities should be calculable additively. In those of Benrath's conductivity curves which exhibit a maximum (A., 1909, ii, 12; 1911, ii, 847), this corresponds practically with the mixture of lowest melting point, and the same

holds for the system AgCl–TlCl, in which the formation of solid solutions is absolutely excluded. The only apparent cause for the increased conductivity lies in the internal friction, which would gradually diminish as the composition of the mixture corresponding with a given isotherm changes so that its melting point is approached. T. H. P.

The Influence of Configuration on the Condensation Reactions of Polyhydroxy-compounds. II. The Effect of Boric Acid on the Conductivity and Specific Rotation of Methylated Derivatives of Mannitol. JAMES COLQUHOUN IRVINE and ETTIE STEWART STEELE (T., 1915, **107**. 1221—1229).—Views formerly expressed as to the configuration of mannitol (T., 1914, **105**, 898) are examined in the light of Böeseken's ideas regarding the conductivity and rotation of polyhydroxy-compounds in presence of boric acid, namely, that exaltation is only observed when two hydroxyl groups are attached to, and are on the same side of, adjacent carbon atoms. That the method is applicable to methyl ethers was shown by the fact that glycerol α-methyl ether gave results similar to those obtained by Böeseken for glycols. The conductivity of various derivatives of mannitol, in which certain hydroxyl groups were substituted and others not, was then examined in aqueous solution and also in $N/2$-boric acid solution. Mannitol showed a marked exaltation of conductivity in boric acid solution as compared with that in aqueous solution, whereas pentamethyl mannitol showed a slight depression. εζ-Dimethyl mannitol and γδεζ-tetramethyl mannitol had much the same effect as mannitol, thus differing from other α-glycols, whilst βγεζ-tetramethylmannitol, mannitolacetone, and mannitoldiacetone gave only a slight depression. Since mannitol, εζ-dimethylmannitol, and γδεζ-tetramethylmannitol behave in a closely similar manner, it must be concluded that the hydroxyl groups 1 and 2, which are common to these three substances, are similarly arranged in each, and are those which react in the positive sense with boric acid. It is shown that the exaltation of rotation due to the action of boric acid on these sugars does not appear to be so useful a criterion of configuration as is the conductivity. T. S. PA.

A Direct Reading Potentiometer for Measuring Hydrogen Ion Concentrations. J. F. MCCLENDON (*Amer. J. Physiol.*, 1915, **38**, 186—190).—The instrument is fully described with diagrams; the hydrogen ion concentration is read directly on a scale and dial. W. D. H.

New Hydrogen Electrodes and Rapid Methods of Determining Hydrogen Ion Concentrations. J. F. MCCLENDON (*Amer. J. Physiol.*, 1915, **38**, 180—185).—Modifications are introduced into the method of Michaelis so that determinations may be made in three minutes; an electrode which eliminates errors due to oxygen from oxyhæmoglobin is described; so also is one which may be lowered into the stomach. W. D. H.

Condition of Carbon Dioxide in the Blood. IV. Electrolytic Dissociation of Sodium Hydrogen Carbonate. E. D'AGOSTINO and G. QUAGLIARIELLO (*Atti R. Accad. Lincei*, 1915, [v]. **24**, i, 858—862. Compare this vol., ii, 426).—The authors have made further measurements of the conductivities of sodium hydrogen carbonate solutions, and give a table showing the degrees of dissociation at 18° and 37° for concentrations ranging from 0 to 0·2 mol. per litre. Almost the only other electrolyte present in appreciable proportion in blood serum is sodium chloride, and the concentrations of solutions of this salt isohydric with those of sodium hydrogen carbonate at 18° and 37° have been calculated from the results of various observers. By means of these numbers, the degree of dissociation of a solution containing known proportions of sodium hydrogen carbonate and chloride may be determined.

T. H. P.

Electromotive Force of Calcium Amalgams. I. and II. LIVIO CAMBI (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 606—611; 1915, **24**, i, 817—822. Compare this vol., ii, 687).—I. The author has measured the *E.M.F.* of calcium amalgams in methyl-alcoholic solutions of calcium chloride cooled to −80°, the solutions being kept in an atmosphere of pure, dry hydrogen. These amalgams exhibit anomalies similar to those observed with sodium amalgams by Haber and Sack (A., 1902, ii, 441), the values of the *E.M.F.* exhibiting oscillations of about 0·08 volt; those containing more than 10 atom. % of calcium give, however, almost or quite constant values. At the composition corresponding with $CaHg_4$, a sudden increase of about 0·2 volt occurs, and in the region 10—15 atom. % of calcium the potential shows another, less sharp variation of about 0·14 volt, this indicating the formation of another compound, possibly $CaHg_9$. Thermal analysis does not reveal the existence of such a compound, possibly because its temperature of formation approximates to the eutectic temperature, −41°, the two arrests being thus superposed.

II. The author has made further measurements of the *E.M.F.* of calcium amalgams and of calcium in methyl-alcoholic solutions of calcium chloride at −80°, similar measurements being also made in pyridine at 25°. In pyridine, calcium amalgams in general show almost constant potentials, these rising gradually to a maximum and then falling; with amalgams containing high proportions of calcium, however, inconstant values are obtained, and with calcium itself the *E.M.F.* diminishes rapidly. Similar results have been obtained by other authors for various metals and amalgams in this solvent. The values of ϵ_H for $CaHg_4$ and Ca at −80° are −1·595 and −1·983 volt respectively.

T. H. P.

Cathodic Deposition of Metals in Presence of Organic Bases. I. Zinc. ARRIGO MAZZUCCHELLI (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 503—508. Compare this vol., ii, 19, 307).—The author has investigated the effect of small proportions of salts of

quinine, cinchonine, quinoline, dimethylaniline, α-naphthylamine, lutidine, aniline, pyridine, and gelatin on the electrolytic deposition of zinc from a solution containing zinc and ammonium sulphates, a pure zinc anode and a brass cathode being used.

With very small proportions of these additions, and when the current density is low, a homogeneous, uniform, fine-grained deposit is obtained. When either the proportion of the added compound or the current density is increased, the zinc separates irregularly in nodular masses. The first uniform deposit invariably dissolves only slowly in hydrochloric acid. It appears that the organic substance present in the neighbourhood of the cathode is absorbed by the metallic granules, which separate initially in a state of high dispersion, and so renders the deposit fine-grained. At a later stage, the organic compound tends to coat the cathode with a more or less impermeable varnish, and thus induces passivity. At certain points of the cathode which are accidentally favoured, deposition may continue at an increased current density, the crystalline, nodular masses being thus formed.

The experiments made up to the present indicate that the cathodic deposition of the zinc is influenced more than the anodic dissolution. It may therefore be supposed that, in a solution of one of these added substances, a zinc electrode would behave unipolarly, as is the case with copper in potassium cyanide solution, and would dissolve irreversibly. It is found, indeed, that passage of an alternating current between two zinc electrodes immersed in a 0·05% quinoline sulphate solution is accompanied by continual evolution of hydrogen, and, further, that the deposition potential of zinc exhibits supertension in presence of one of the above bases. Possibly such addition of a base may result in the electrolytic deposition of alloys which are not formed from the pure solutions. T. H. P.

Measurements of the Cathodic and Anodic Polarisation of Metals in Presence of Organic Bases. I. Zinc. ARRIGO MAZZUCCHELLI (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 626—633).—Organic bases, such as quinoline and quinine, which in the form of salts influence, usually unfavourably, the cathodic deposition of zinc (compare preceding abstract), exert a correlative action on the electrolytic potential of this metal, increasing both the cathodic and the anodic polarisability. Gelatin exhibits an analogous, but less marked, effect. T. H. P.

Electrolytic Formation of Bronze. W. D. TREADWELL and E. BECKH (*Zeitsch. Electrochem.*, 1915, **21**, 374—380).—Experiments are described which were made with the object of ascertaining the tendency of copper and tin to form alloys. Alternate layers of copper and tin were electrolytically deposited on a platinum cathode, and the dried deposit was heated at the melting point of tin in the absence of air. There was in no case a formation of bronze. A number of electrolytic baths which have previously been described for the production of bronzes were

controlled, and in all cases shown to be inefficient. Three new electrolytic baths were then constructed and examined, potential differences being determined in all cases for both of the metals. The bath consisting of copper and zinc in an alkali hydroxide and cyanide solution proved to be unsatisfactory. A solution composed of 50 grams of copper sulphate, 104 grams of potassium cyanide, and 70 grams of potassium hydroxide was mixed with a solution of 37 grams of potassium oxalate and 82 grams of tin potassium chloride. The whole was made up to a volume of 2 litres, and cleared by the addition of a small quantity of potassium hydroxide. The clear solution, when electrolysed at 40° with a cathode current density of 1—2 amperes per 100 sq. cm., yielded reddish bronzes. A further electrolytic bath of hydroxide, cyanide, and sulphide complexes of copper and tin yielded golden bronzes. J. F. S.

Specific Heat of Platinum at High Temperatures. Luigina Fabaro (*Nuovo Cim.*, 1915, [vi], **9**, i, 123—139).—The author has investigated, by a method differing somewhat from that used by Corbino in his experiments on tungsten (A., 1912, ii, 327, 531), the change in temperature in an incandescent platinum filament in consequence of the sudden suppression of a small resistance contained in the circuit, the specific heat of the metal being calculated from the results obtained. The following table shows the relations between the resistance of the filament, its temperature, and the specific heat, in arbitrary units, at constant volume and at constant pressure:

R.	T.	c_v.	c_p.
4·07	980°	1·118	1·206
4·58	1178	1·166	1·273
4·99	1353	1·187	1·309
5·17	1440	1·213	1·344
5·37	1543	1·240	1·382

The values of c_v are calculated from those of c_p by means of the Nernst and Lindemann formula, which, for platinum, Corbino expresses in the form $c_p = c_v[1 + 63 . 10^{-6}(T + 273)]$.

The above numbers show that, even at high temperatures, the specific heat of platinum increases with rise of temperature, this result being in disagreement with the general theory, according to which the specific heat should be constant at such temperatures.

T. H. P.

Entropy in Solid Substances and its Relations to other Physical Magnitudes. Stefano Pagliani (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 835—841).—The author has calculated, by means of the expression given by Planck, $S = \int_0^T c_p/T . dT$ (A., 1912, ii, 230), the values of the absolute entropy at the melting point for those simple and compound solid substances for which experimental data on specific heats are available. The numbers thus obtained show that, for the elements, the value of the entropy at the melting point tends to diminish as the atomic weight increases. This relation holds exactly for the members of the separate groups of

Mendeléev's system, when the metals are classified apart from the non-metals. But, even in any separate group, the products of entropy and atomic weight are not constant. Tammann's assertion (A., 1913, ii, 1022) that the entropy per gram-atom in the metals before fusion is independent of the metal is, therefore, inaccurate. This result is discussed in relation to modern atomistic doctrines.

For the frequency of the atomic vibratory motion, Lindemann gives the expression $\nu = k\sqrt{(T/mV^{\frac{2}{3}})}$, where k is a coefficient determined empirically, T the absolute melting point, m the atomic mass, and V the atomic volume. From this it follows that the values of the frequency should diminish with increase of the atomic weight. The author has calculated the values of ν for the elements, and finds that the metals may be divided into three classes, according to the value of the ratio of the entropy to the atomic vibratory frequency: (I) the alkali metals, for which S/ν has the mean value 0·36; (II) the metals of the second, third, fourth, and sixth groups, and the first series of the eighth group of the periodic system, for which S/ν has the mean value 0·146; (III) those of the fifth group and of the second series of the eighth group, for which S/ν has the mean value 0·10. The non-metals (IV) form a separate class, the mean value of S/ν being 0·22. Consequently, the frequency of the atom in different substances may be calculated by multiplying the entropy by a factor of proportionality, this being obtained by dividing the coefficient of Lindemann's formula by the corresponding mean value of S/ν. To this coefficient different values have been ascribed, the one most generally adopted being $2{\cdot}12 \cdot 10^{12}$; this would give, for the proportionality factors corresponding with the above four classes of elements, the values: (I) 6·0; (II) 14·5; (III) 21·2; and (IV) 9·6.

The values of the atomic vibratory frequency calculated by means of these factors are in satisfactory agreement with those obtained in other ways, excepting with gold, platinum, and sulphur. The author's values for platinum and gold are possibly somewhat low, owing to the extent of the extrapolation employed to deduce the specific heats. In the case of sulphur, the divergences are reconcilable by regarding rhombic sulphur (and graphite) as polyatomic, so that two frequencies should be introduced into Einstein's formula and into that of Nernst and Lindemann. Further, the value of the entropy for sulphur may be brought into line with those of the other elements by assuming that it has the doubled atomic weight, 64·14, the frequency found by Nernst being almost exactly double that calculated by the author. T. H. P.

Critical Temperature of Mercury. Julie Bender (*Physikal. Zeitsch.*, 1915, **16**, 246—247).—According to Koenigsberger (A., 1912, ii, 1134), the critical temperature of mercury is about 1270°, but Menzies (A., 1913, ii, 864) considers this temperature to be much too low. Further experiments have now been made in which mercury was heated in sealed quartz tubes, and the changes in volume of liquid and vapour phases observed up to 1400°. In different experiments, the ratio of the volume of the mercury to

that of the quartz tube was varied considerably. In order to obtain the density of the saturated vapour at high temperatures, similar tubes were heated, and the temperature at which the liquid just disappeared was determined. From the data obtained in this way, the orthobaric densities can be deduced, and the curves plotted from these indicate that the critical temperature must be lower than 1650°. It is higher than 1500°, for in one experiment the temperature was raised to this value, and liquid mercury was still present. H. M. D.

Determination of Melting Point. R. Romanelli (*Ann. Chim. anal.*, 1915, **20**, 178; from *Giorn. farm. chim.*, 1915, 151).—A loop, 8 or 9 mm. in diameter, is formed at one end of a thin platinum wire, and the other end of the wire is wound spirally round the bulb of a thermometer. The substance under examination is melted, and the loop is dipped into it; a film of the substance is retained in the loop when this is withdrawn. After cooling for one hour, the wire and the thermometer are immersed in cold water, and the temperature of the latter is raised gradually. The point at which the film is ruptured is taken as the melting point of the substance. W. P. S.

A Possible Cause of the Doubling of the Raoult Effect in Dilute Solutions of Electrolytes. Emil Kohl (*Chem. Zentr.*, 1915, **86**, i, 1147; from *Sitzungsber. K. Akad. Wiss. Wien.*, 1914, **123**, II*a*, **26**, 3—12).—The author has calculated the internal energy and from this the entropy and the free energy in definite form, from the equation of condition of a substance. The last-named quantity allows of the representation of the equilibrium conditions of the thermodynamic potential in terms which contain only defined energy functions. From this the laws, which are characterised as the Raoult effect, that is, the lowering of the vapour pressure and freezing point, and the elevation of the boiling point, can be very simply evolved. As an explanation of the known anomalies of these effects in dilute solutions of electrolytes, the ionisation theory is unnecessary, but they can be explained on the assumption of a special form of equation of condition, for example, that of Eisenmann (*Ber. Deut. physikal. Ges.*, 1912, **14**, 769). The doubling of the effects is therefore due to the electromagnetic vibrations of the molecule. J. F. S.

Heats of Formation of the Compounds formed in the Conversion of Carbon into Gas. Fritz Hoffmann (*Zeitsch. angew. Chem.*, 1915, **28**, 322—324).—In view of the disadvantages which are involved in the use of slightly different values for the heats of combustion of carbon, carbon monoxide, and hydrogen, the author recommends the general use of the following data: $C + O_2 = CO_2 + 96960$; $CO + O = CO_2 + 68200$; $H_2 + O = H_2O$(vapour, 0°) + 57820 or $H_2 + O = H_2O$(liquid, 0°) + 68630 cal. H. M. D.

Heats of Dilution of Concentrated Solutions. Wm. S. Tucker (*Phil. Trans.*, 1915, [*A*], **215**, 319—351).—A simple form of

calorimeter is described, which has been employed in the measurement of the specific heats and heats of dilution of concentrated aqueous solutions.

The results obtained with hydrochloric acid solutions of varying concentration show that the specific heat s varies with the concentration n (expressed in terms of the number of mols. of acid per 100 mols. of water) in accordance with the equation $s.n^{\frac{1}{4}}=1{\cdot}277$. This equation holds for values of n between 22·8 and 7·7, but is not applicable to more dilute solutions.

In dealing with the heats of dilution, the author makes use of the differential heat of dilution, which may be defined as the quantity of heat which is liberated or absorbed when one mol. of water is added to an infinite quantity of solution. If N is the number of mols. of water per mol. of solute in the solution under examination, the differential heat of dilution may be represented by dQ/dN. It is found that the results obtained by the author from his experiments on solutions of hydrochloric acid, lithium chloride, and sodium hydroxide, and those obtained by Thomsen for other concentrated solutions, can be represented by an equation of the form $dQ/dN=A/N+B$. For hydrochloric acid ($N<10$), $A=4082$, $B=-272{\cdot}1$; nitric acid ($N<6$), $A=2020$, $B=0$; sulphuric acid ($N<15$), $A=4666$, $B=-196$; hydrobromic acid ($N<10$), $A=3356$, $B=0$; acetic acid ($N<10$), $A=-63{\cdot}49$, $B=40{\cdot}84$; sodium hydroxide ($N<6$), $A=-7840$, $B=-980$; lithium chloride ($N<6$), $A=6968$, $B=-871$; ammonium nitrate ($N<10$), $A=-1172$, $B=48{\cdot}77$.

The data for hydrochloric acid solutions show that the heat of dilution rises with the temperature, whilst for lithium chloride solutions the heat of dilution is nearly independent of the temperature. The results obtained in the measurement of the heat of dilution of the concentrated solutions seem to show that the solute is dissolved in some definite hydrate which, in general, contains a large number of molecules of water. In the case of acetic acid, however, the number of molecules of water in the hydrate would appear to be small, and the solvent is said to be pure water when the solute is nitric or hydrochloric acid. H. M. D.

The Properties of Cold-worked Metals. II. Methods of Measuring Small Changes of Density produced by Annealing. Reginald George Parker and Thomas Martin Lowry (T., 1915, **107**, 1160—1168. Compare this vol., ii, 611).—The authors describe the experimental methods which have been developed in the course of their work on the properties of cold-worked metals (T., 1915, **107**, **1005**). The pyknometers used to measure the densities of metallic filings were small silica flasks, having a capacity of 5—7 c.c., and a capillary neck of 1 mm. bore. They had the advantage that their weights remained constant within 0·0001 gram on every weighing when in constant use over many months. Moreover, no change was produced in the weight or capacity of the flasks by ignition, so that it was possible to anneal many of the metals in the flasks. The filling liquids which were found to be satisfactory were ethylene

bromide (D 2·18) for gold, silver, copper, cadmium, and cadmium-silver alloy, and carbon tetrachloride (D 1·6) for tin, bismuth, antimony, zinc, and magnesium. The pyknometers were calibrated by filling with water and weighing to 0·05 mg., every care being taken to make the temperature adjustment accurate.

The dilatometers used are described, together with the method of filling them. The difficulty which arises with sensitive dilatometers in maintaining the temperature sufficiently constant to prevent casual movements of the meniscus was overcome by making all the measurements differentially with two dilatometers, one containing the metal and filling liquid, and the other containing the liquid alone. The most satisfactory filling liquid was found to be paraffin fractionated out from commercial kerosene, using the portion boiling between 245° and 280°, after certain preliminary treatment with chromic acid. For temperatures between 240° and 260° a fraction of higher boiling point was used, but at 260° gassing took place with cobalt and silver, the only two metals which did not gas at 240°. The dilatometers were heated in the vapour of liquids boiling at temperatures varying from 80° to 261°. The thermometer action in the dilatometers is discussed, and a full description given of the method of dealing with it and of the corrections to be employed in making the measurements.

Fresh data are given with respect to the densities of dental alloy, silver-cadmium alloy, and copper, using the pyknometric method.

T. S. P.

The Co-volume of Gases Evolved by Explosive Substances. Daniel Berthelot (*Compt. rend.*, 1915, **161**, 209—211).—Sarrau's relationship between the co-volume and the specific volume of gases (compare *Compt. rend.*, 1882, **94**, 847), as applied by Mallard and Le Chatelier (*Mém. Poudres et Saltpêtres*, 1884—1889, **2**, 144) to the gases from explosive substances which have a simple molecular structure and are relatively stable at high temperatures, may hold good in such cases, but it must not be considered to have general application. Using his own equation of state, the author shows that the co-volume is only equal to 1/1000th the specific volume for gases for which the critical temperature is approximately equal to four times the critical pressure. W. G.

Temperature-coefficients of Surface Tension in Binary Mixtures. M. Padoa and A. Matteucci (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 590—595).—Further experiments have been made on the determination of the degree of association between solvent and solute by means of the surface tension (compare Padoa and Tabellini, A., 1914, ii, 252), the following cases being investigated: (1) mixtures of two non-associated solvents; (2) mixtures of an associated with a non-associated liquid; (3) solutions of solids in non-associated solvents. This question has received attention from Ramsay and Aston (A., 1895, ii, 40) and from Worley (T., 1914, **105**, 260, 273); the numbers obtained by the latter lead to temperature-coefficients of the surface tension indicating associa-

tion in pure water and pure phenol, and in mixtures of water with phenol or aniline.

The surface tensions of the following mixtures have been measured at various temperatures. Benzene and toluene: no sign of association is evident here, although the densities of the mixtures are higher than those of the components. Benzene and *cyclo*hexane: the latter compound is perhaps slightly associated in the pure state, and the mixtures also exhibit association to some extent. Benzene and naphthalene: slight association. Benzene and phenol: in general, the mixtures are more highly associated than the pure components, and the association constant exhibits a maximum for approximately equimolecular mixtures. T. H. P.

Adsorption Capacity of Peat. PAUL ROHLAND (*Kolloid. Zeitsch.*, 1915, **16**, 146—148).—Peat adsorbs many dyes very readily from aqueous solution. Starch and colloidal ferric hydroxide are also adsorbed by peat, although not so readily as by colloidal clays and clay soils. Ions are not adsorbed. H. M. D.

An Experiment of J. J. Thomson on the Dissociation of Iodine Vapour by the Passage of Electric Sparks. W. KROPP (*Zeitsch. Elektrochem.*, 1915, **21**, 356—359).—Sir J. J. Thomson (A., 1887, 1013) has shown that iodine vapour when subjected to electric sparks is dissociated to an extent of 47%, and the dissociation persists for long periods. The author has repeated the experiment, using a spiral glass manometer of the type used by Preuner and Schupp (A., 1909, ii, 977), and has been unable to show that any dissociation occurs at temperatures up to 135°. J. F. S.

Disposition of the Atoms in Crystals. A. JOHNSEN (*Physikal. Zeitsch.*, 1915, **16**, 269—272).—A discussion of the symmetry relations of crystal structures with reference to the results of the determination of the disposition of the atoms by *X*-ray methods. It is possible to determine the number of symmetrically disposed atoms for each of the thirty-two groups of crystals, and in this way to determine to what extent the several atoms of a particular element in a compound are structurally equivalent. Thus it may be shown that the five atoms of chlorine in phosphorus pentachloride, the seven oxygen atoms of the water of crystallisation in $FeSO_4,7H_2O$, the three oxygen atoms in arragonite, the four fluorine atoms in zirconium fluoride ($ZrF_4,3H_2O$), the six nitrogen atoms in luteocobaltic chloride, $[Co(NH_3)_6]Cl_3$, are not equivalent in their structural relations. On the other hand, it is possible that the six chlorine atoms in tungsten hexachloride are similarly disposed in the crystal structure. H. M. D.

General Equations for the Neutralisation of Dibasic Acids and their Use to Calculate the Acidity of Dilute Carbonate Solutions. E. B. R. PRIDEAUX (*Proc. Roy. Soc.*, 1915, [*A*], **91**, 535—543).—The conditions of equilibrium in aqueous

solutions containing weak dibasic acids and the corresponding salts have been examined, and equations derived which show the relation between the hydrogen ion concentration and the ratio of acid to base. The equations are applied to dilute carbonate solutions, for which numerous experimental data are available. H. M. D.

Velocities of Phototropic Transformations and their Temperature-coefficients in Monochromatic Light. M. PADOA and A. ZAZZARONI (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 828—835).—It has been shown by Padoa and Minganti (A., 1914, ii, 191) that the processes of coloration in the light of salicylidene-β-naphthylamine and benzaldehydephenylhydrazone are unimolecular reactions, whilst the decolorations of these compounds when heated are bimolecular.

Similar measurements have been made with sodium diacetyl-*pp'*-diaminostilbene-*oo'*-disulphonate (compare Stobbe and Mallison, A., 1913, ii, 459). The velocity of coloration by sunlight at the ordinary temperature is that of a bimolecular reaction, and its temperature-coefficient per 10° is 1·07. At temperatures ranging from 76° to 100°, the decolorisation is unimolecular, and the temperature-coefficient of the velocity about 1·65. The coloration may be assumed to correspond with a polymerisation and the decolorisation with a depolymerisation, the equilibrium being defined by the equation $K'x = K''I(1-x)^2$, where I is the intensity of the light.

In monochromatic, blue light (λ 478—410), the coloration is also bimolecular, but, owing to the greater stability of its red modification, salicylidene-β-naphthylamine was used in further experiments in this direction. In these, green, blue, and violet lights were employed, and the coloration is found to be a unimolecular reaction in each case. The temperature-coefficients of the velocity per 10° are: white light (between 0° and 30°), 1·42; green, which is the least active (40° and 70°), 1·80; blue, which acts most rapidly (40° and 70°), 1·45; and violet, 1·39. With white light, the increment of the velocity with the temperature is virtually that of the most active constituent of the light. Trautz (A., 1908, ii, 339) has pointed out that photochemical processes activated by light of high wave-length should be characterised by high temperature-coefficients of velocity, whilst reactions sensitive to light of small wave-length should have coefficients approximating to unity. These theoretical conclusions are confirmed by the authors' results. T. H. P.

Connexion between Electrolytic and Pure Chemical Processes. IV. D. REICHINSTEIN (*Zeitsch. Elektrochem.*, 1915, **21**, 359—372. Compare A., 1913, ii, 843; 1914, ii, 23; this vol., ii, 245).—A very large number of experiments have been carried out on the velocity of solution of nickel in mixtures of sulphuric acid and hydrogen peroxide, and sulphuric acid and chromic acid, with the object of ascertaining the main causes of chemical polarisation (passivity). In the case of sulphuric acid and hydrogen peroxide, the velocity of solution of nickel rises rapidly to a maximum, and

then falls again to zero. This, when the concentration of the acid solution is kept constant by using large volumes, is explained by surface phenomena and by a gradual conversion of the metal into the passive condition. A piece of nickel which has been rendered passive by immersion in a 3% solution of hydrogen peroxide becomes active again when placed in 0·04*N*-H_2SO_4 containing hydrogen peroxide; a very high maximum velocity of solution is rapidly reached, and then the nickel slowly becomes passive again with a falling off of the velocity of solution, this despite the fact that the concentration of the solution is kept constant. There are two passive conditions of nickel, the one depending on a high concentration of molecular oxygen and a low concentration of atomic oxygen in the electrode volume, and the other on a low concentration of molecular oxygen and a high concentration of atomic oxygen in the electrode volume. In chromic acid solution, other things being the same, nickel becomes passive much more rapidly and at much smaller concentrations than in hydrogen peroxide solutions. This is to be explained by a more rapid formation of atomic oxygen in the chromic acid solution than in the hydrogen peroxide solution. The rate of solution of nickel in chromic acid reaches a constant value. This is defined by its being reached both from the active and passive forms of nickel. The fact that the activation of a nickel plate after the stationary velocity of solution has been reached yields a higher solution velocity than the stationary value is taken to indicate a confirmation of the ballast theory. The slow conversion of nickel into the passive condition is explained by a slow loading of the electrode volume with molecular oxygen. The theory of the driving back of the velocity has been considered mathematically, and, omitting third-power quantities, the velocity at the stationary condition is given by the parabolic function $v_s = k_1 z - k_2 z^2$, in which v_s is the velocity at the stationary point, k_1 and k_2 are constants, and z is the concentration of the oxidising agent in the solution. The major portion of the velocity concentration curve calculated from this expression coincides with the curve found experimentally. J. F. S.

Partition Coefficient and Extraction Velocity of Some Organic Acids. Joh. Pinnow (*Zeitsch. anal. Chem.*, 1915, **54**, 321—345).—The author has made a large number of experiments and tabulated the results. The partition coefficients between water and ether are given for acetic acid at 15°, for malic and succinic acids at 15°, 20°, and 25·5°, for citric, tartaric, lactic, and oxalic acids at 15° and at 25·5—27·5°; in the latter case, also, in the presence of sulphuric acid.

The extraction velocity of these acids from aqueous solutions of varying volume by means of ether, eventually in the presence of sulphuric acid, has been determined in the Partheil-Rose apparatus. When experimenting with acetic acid, this should be strongly diluted.

The extraction, which practically follows the formulæ for unimolecular reactions, is, within certain limits, inversely proportional

to the volume extracted, and also approximately so to the partition coefficient for 27°. If the partition coefficients of the above acids at 27° are divided by 0·04, there is obtained the time in minutes sufficing for the practically complete (99%) extraction from 30 c.c. of liquid in the Partheil-Rose apparatus. Oxalic acid solutions should be mixed with sulphuric acid up to 1/6 molar; a smaller amount of that acid is also advisable for the other acids.

L. DE K.

The Velocity of Nitration of Benzene and Some of its Derivatives. J. P. WIBAUT (*Rec. trav. chim.*, 1915, **34**, 241—258).—The author has determined the velocities of nitration of benzene, toluene, chlorobenzene, and bromobenzene in solution in acetic anhydride, the nitration of toluene being carried out at 0° and of the other three at 25°. The strength of the solutions with respect to the substance to be nitrated was in each case approximately $N/2$. The results show that, using an excess of nitric acid, the nitration of benzene and chlorobenzene is governed by the laws of bimolecular reactions. In the case of bromobenzene, the value of the velocity constant tends to increase as the reaction proceeds. No satisfactory mean value could be obtained for the velocity constant in the case of toluene. Taking the results as a whole, they show that these four substances can be arranged in descending order of velocities of nitration, as follows:

$$C_6H_5\cdot CH_3 > C_6H_6 > C_6H_5Cl > C_6H_5Br.$$

The results are not in agreement, as far as chloro- and bromobenzene are concerned, with the hypothesis of Böeseken and Holleman ("Die direkte Einführung," 1909) on substitution in the benzene nucleus. W. G.

Types of Substitution. A. F. HOLLEMAN (*Rec. trav. chim.*, 1915, **34**, 259—260).—In view of Wibaut's results (compare preceding abstract), the author considers it necessary to modify slightly his hypothesis on substitution in the benzene nucleus (compare "Die direkte Einführung"), and admits that the introduction of a substituent can considerably modify the velocity with which the five remaining hydrogen atoms can be substituted, but that there still remains a great difference between the velocity with which the atoms 2, 4 and 3, 5 are substituted. W. G.

Activation of Hydrogen and Oxygen by Platinum. J. EGGERT (*Zeitsch. Elektrochem.*, 1915, **21**, 349—352. Compare A., 1914, ii, 638).—Experiments have been carried out with the object of determining the amount of hydrogen absorbed by a ferric salt in the presence of platinum under different conditions of stirring, and with the platinum totally and partly immersed in the solution. Similar experiments were carried out on the absorption of oxygen by quinol solutions, and the absorption of hydrogen by *p*-benzoquinone solutions. It is shown that the maximum velocity effect in the activation of hydrogen and oxygen toward metal solutions which are capable of reaction is due to a contact

action of the platinum which takes place in the presence of undissolved gas and solution when these form a surface layer on the catalyst. Hydrogen is capable of distributing itself in platinised platinum, and can exert a chemical influence in places other than the point of occlusion. The connexion between this action and that of a gas electrode is discussed. Henry's law holds for the activation of hydrogen and oxygen at pressures from 0·25 to 4 atmospheres. Electrolytically deposited platinum and palladium have practically the same activating power, whereas colloidal solutions of these metals have a much greater activity, on account of the greater surface presented by these solutions. J. F. S.

Catalytic Influence of [Glass] Vessel Walls. GEORG VON ELISSAFOV (*Zeitsch. Elektrochem.*, 1915, **21**, 352—356).—The catalytic effect of glass wool of various sorts and sea sand in the presence of various metallic salts has been studied by measuring the rate of decomposition of hydrogen peroxide. From the experiments, an attempt is made to deduce the connexion between adsorption and catalytic activity. It is shown that the rate of decomposition of hydrogen peroxide in the presence of glass wool is further increased by the addition of a salt of a heavy metal ($CuSO_4$), and by an amount which is far greater than the sum of the two individual effects. The catalysis by glass wool and a heavy metal salt ($CuSO_4 : MnSO_4$) follows the conditions of a reaction of the first order. The adsorption of copper sulphate by glass wool of Jena glass follows the simple adsorption isothermal for low concentrations, but with higher concentrations saturation occurs. The velocity of decomposition of hydrogen peroxide by Jena glass wool and copper sulphate is proportional to the amount of copper sulphate adsorbed by the glass wool. J. F. S.

Catalysis. XXI. Reactions of both the Ions and the Molecules of Acids, Bases, and Salts. Reactions of Sodium Ethoxide with Methyl Iodide in Absolute Ethyl Alcohol at 25°. H. C. ROBERTSON, JUN., and S. F. ACREE (*J. Amer. Chem. Soc.*, 1915, **37**, 1902—1909).—A study of the above reaction along the lines of previous work (A., 1913, ii, 688, etc.) shows that the deviation from a purely ionic reaction is proportional to the concentration of sodium ethoxide, and that the effect of the sodium iodide and ether produced on the velocity of the reaction is very small. The same reaction was the subject of a paper by Shroder and Acree (T., 1914, **105**, 2582), and the theoretical considerations were developed in that place. J. C. W.

Catalysis. XXII. Reactions of both the Ions and Molecules of Acids, Bases, and Salts. A Re-interpretation of the Reactions of Sodium Methoxide and Sodium Ethoxide with *o*-Dinitrobenzene, 4-Chloro-1 : 2-dinitrobenzene, and 4-Bromo-1 : 2-dinitrobenzene. S. F. ACREE (*J. Amer. Chem. Soc.*, 1915, **37**, 1909—1914).—Reactions of the above type, which have been recognised as non-ionic, illustrate very well the author's

theory that the deviation from the ionic reaction is not due to "salt catalysis," but is proportional to the concentration of the molecular sodium alkyloxide. The values of K_v, recalculated from the author's equation $K_v = K_i\alpha + K_m(1-\alpha)$, using the data of Bruyn, Steger and Luloffs (A., 1899, i, 745; 1902, i, 87; 1905, ii, 150), are in close agreement with the values actually found.

J. C. W.

The Quantum Theory of Radiation and the Structure of the Atom. N. Bohr (*Phil. Mag.*, 1915, [vi], **30**, 394—515. Compare A., 1913, ii, 689, 943, 1045).—Certain points connected with the author's theory of atomic structure are examined more closely, with special reference to recent experimental work bearing on the question. The evidence afforded by recent observations on line spectra and characteristic Röntgen rays is shown to afford considerable support to the main principles of the quantum theory. In particular, it is shown that the results obtained by Stark for the effect of an electrical field on the hydrogen spectrum are in satisfactory agreement with those derived on the basis of the author's theory.

The general formula (*Phil. Mag.*, 1914, [vi], **27**, 506) for the energy of the series of stationary states for systems which contain more than one electron cannot be interpreted in detail, but it is shown that this formula is not only supported by Stark's experiments on the effect of electrical fields, but also by measurements of the minimum voltages which are necessary to produce spectral lines, and by the relations which have been found as the result of the examination of the high-frequency spectra of the elements.

H. M. D.

Experiments Indicating the Structure of the Molecule. C. A. Crommelin (*Chem. Weekblad*, 1915, **12**, 714—729).—A historical survey of research on molecular structure. A. J. W.

Diameter of Molecules and Molecular Weight. W. Herz (*Zeitsch. Elektrochem.*, 1915, **21**, 373).—The author has calculated the diameter of the molecules of a number of alcohols, acids, and hydrocarbons by means of the equation $\rho = 2\gamma v/L$, in which ρ is the diameter of the molecule, γ the capillarity constant, v the volume of 1 gram of the substance, and L the heat of vaporisation of the same quantity. It is shown that in all cases the diameter is of the order $1{\cdot}0 \times 10^{-8}$ cm., but it increases with increasing molecular weight. That it does not depend only on molecular weight is shown by the fact that isomerides have different diameters in many cases. The difference in the diameter of isomerides is greater the greater the difference in constitution. J. F. S.

Use of Acetone for Drying Chemical Utensils. O. L. Barnebey (*J. Amer. Chem. Soc.*, 1915, **37**, 1835).—Rinsing with acetone instead of with alcohol and ether is recommended.

J. C. W.

Inorganic Chemistry.

Molecular Weight of Water in the Form of Saturated Vapour from − 20° to 270°. Spontaneous Ionic Dissociation of Water Vapour. I. GIUSEPPE ODDO (*Gazzetta*, 1915, **45**, i, 319—338. Compare this vol., ii, 520).—Application of Avogadro's law, which is valid for saturated vapours, to the determination of the volume, pressure, and temperature corresponding with a given weight of saturated water vapour shows that the molecular weight has the value 18·016, corresponding with the simple molecule, only at 32°. As the temperature rises from 32°, the molecular weight continuously increases, association into H_4O_2 taking place; at 270° the percentage of association is 41·41. Fall of the temperature below 32° is accompanied by diminution of the molecular weight, owing to the spontaneous ionic dissociation of the water vapour. These two opposed phenomena, which are continuous and overlap within certain limits, are functions of the concentration, and depend on Le Chatelier's law of mobile equilibrium. T. H. P.

Action of Chlorine on Sodium Thiosulphate. P. A. W. SELF (*Pharm. J.*, 1915, **95**, 133–134).—Experiments were made on the action of chlorine on solutions of sodium thiosulphate, both in presence and absence of alkali, with the object of determining the proportion of free acid formed in the interaction with the thiosulphate, and the amount of alkali which must consequently be added to render a respirator solution most effective. The results indicated that an amount of sodium carbonate, $Na_2CO_3,10H_2O$, slightly in excess of the amount of thiosulphate, must be present in order that the solution may remain alkaline until the whole of the thiosulphate has been decomposed by the chlorine. For the attainment of maximum efficiency of a respirator solution, therefore, the author recommends the use of 60 parts of crystalline sodium carbonate to 52 parts of thiosulphate and 100 of water. This formula is very different from that recommended by the Paris Academy of Medicine, and experiments conducted on a solution made to their formula showed that it became acid, and therefore useless, when only 35% of the thiosulphate had been decomposed. G. F. M.

Hardness and Microstructure of Fusions of Tellurium and Sulphur Compounds. P. SALDAU (*Jahrb. Min.*, 1915, ii, *Ref.* 21; from *Ann. Inst. Mines, St. Pétersb.*, 1913, **4**, 228—237).—The curve of hardness for the system Pb–Te shows for the compound PbTe (altaite) a hardness of 31·85 kg./mm.^{2}, considerably in excess of that of either of the components (Pb 3·92, Te 18·43 kg./mm.^{2}). The maximum degree of hardness (33·58 kg./mm.^{2}) corresponds with a content of Te 49·8 atomic %. In the system PbTe–Pb, lead telluride enters into solid solution only to a limited extent, whilst

in the system PbTe–Te it fails. Lead sulphide enters into solid solution, but not exceeding 2%, in the systems PbS–FeS, PbS–Ag_2S, and PbS–Cu_2S. The system PbS–PbTe does not form a continuous isomorphous mixed series. L. J. S.

Reduction of Phosphorus Haloids. I. Action of Mercury on Phosphorus Haloids. Preparation of 100% Red Phosphorus. Ludwig Wolf (*Ber.*, 1915, **48**, 1272—1280).—The interaction of phosphorus tribromide and mercury, with formation of mercuric bromide and red phosphorus, is reversible, the reverse process being favoured by high temperature and low pressure. When a mixture of mercury and phosphorus tribromide is heated in a sealed tube at 100—170° for several days, the resulting product extracted with ether, and the residue again heated with phosphorus tribromide, there is obtained a pure red phosphorus as a cinnabar-red, micro-crystalline powder, D_4^{24} 1·876, which becomes brownish-black at 250°, and regains its colour on cooling; it is insoluble in carbon disulphide, is not blackened by ammonia (compare Schenck, A., 1903, ii, 363; Stock and Johannsen, A., 1908, ii, 583; Stock, Böttcher and Lenger, A., 1909, ii, 728), is indifferent to liquid air, oxidises slowly in moist air, and inflames in air at approximately 300°. The different behaviour of the red phosphorus described by Schenck is attributed to the presence of yellow phosphorus.

The formation of mercuric bromide and phosphorus in this way is probably preceded by the formation of mercurous bromide and half the final quantity of phosphorus as an intermediate stage of the reaction. The reverse process can be demonstrated by heating at 240° a mixture of the pure red phosphorus and mercuric bromide in one arm of a bent sealed tube, when phosphorus tribromide will slowly condense in the other arm if this is cooled in a freezing mixture.

Phosphorus trichloride does not behave in exactly the same manner as the tribromide towards mercury, because the reaction in this case ceases at the stage involving the formation of mercurous chloride, so that the reaction product contains this substance and red phosphorus; an explanation of the failure of the reaction to proceed further may be present in the fact that the interaction of phosphorus trichloride and mercurous chloride would involve an endothermic chemical change. D. F. T.

Gaseous Combustion at High Pressures. William Arthur Bone, Hamilton Davies, H. H. Gray, Herbert H. Henstock, and J. B. Dawson (*Phil. Trans.*, 1915, [*A*], **215**, 275—318).—By means of an apparatus specially designed to withstand high pressures, the authors have investigated the behaviour of a number of gaseous mixtures when exploded at constant volume and high initial pressure (10 to 50 atmospheres). From experiments in which mixtures of methane and hydrogen, or methane and carbon monoxide, were exploded with a quantity of oxygen insufficient for complete combustion, data have been obtained from which conclusions are

drawn respecting the relative affinities of these gases for oxygen in flame combustion.

Experiments in which mixtures of methane and oxygen varying from $2CH_4 + O_2$ to $CH_4 + O_2$ were exploded show: (1) that steam and the oxides of carbon are present in the products formed from all these mixtures; (2) that large quantities of both carbon and steam are formed in the explosion of the mixture $2CH_4 + O_2$; (3) that carbon disappears from the products when the proportion of oxygen in the exploded mixtures exceeds 40%. The observations are interpreted in terms of the hydroxylation theory. For the mixture $CH_4 + O_2$, the primary oxidation may be represented as $CH_4 + O_2 = H_2{:}C{:}(OH)_2 = H_2{:}C{:}O + H_2O = H_2 + CO + H_2O$. In the case of the mixture $2CH_4 + O_2$, it is supposed that half the molecules of methane are primarily transformed into $CH_2(OH)_2$, and that the heat liberated by this change is sufficient to decompose a portion of the remaining methane into its elements. When the intermediate mixture $3CH_4 + 2O_2$ is exploded, one-third of the methane is supposed to be directly transformed into $CH_2(OH)_2$, and the remaining two-thirds into $CH_3{\cdot}OH$. Neither of these deposits carbon during the subsequent thermal decomposition.

The explosion of mixtures of methane and hydrogen with insufficient oxygen for complete combustion gave the following results for the mean distribution of the oxygen between the two gases. The numbers show the percentage of the oxygen used up by the methane. The distribution varies with the size of the explosive bomb used, and this is, no doubt, due to the influence of the walls of the containing vessel. The numbers in brackets refer to explosions carried out with a larger bomb. Mixture $CH_4 + O_2 + 2H_2$, 95·34% (97·1%); $CH_4 + O_2 + 4H_2$, 81% (91%); $CH_4 + O_2 + 6H_2$, 54·9% (72·6%); $CH_4 + O_2 + 8H_2$, 31·4% (—).

From the results obtained with the mixture $CH_4 + O_2 + 2H_2$, the conclusion is drawn that the affinity of methane for oxygen in explosions is at least twenty to thirty times greater than that of hydrogen. For a given explosion vessel, the influence of successive increases in the ratio of hydrogen to methane on the distribution of oxygen is proportional to the square of this ratio. This is considered to indicate that hydrogen in explosions is directly burnt to steam as the result of termolecular impacts, as represented by the equation $2H_2 + O_2 = 2H_2O$.

Similar experiments with mixtures of methane and carbon monoxide gave the following for the proportion of oxygen used up by the methane: $CH_4 + O_2 + 3CO$, 91·5%; $CH_4 + O_2 + 2CO$, (95·3%). These results would seem to show that carbon monoxide is more effective than hydrogen when in competition with methane for a limited supply of oxygen.

The results obtained in the explosion of mixtures of ethylene and hydrogen with oxygen, and of ethane with its own volume of oxygen, are also recorded.

In the final section of the paper an account is given of the pressure curves which were obtained when methane, hydrogen, and carbon monoxide were separately exploded with a quantity of air

sufficient to complete the primary oxidation. The data obtained show that there is no apparent connexion between the relative rates at which the maximum pressure is developed and the relative affinities of the respective gases for oxygen. H. M. D.

Binary and Ternary Systems of the Nitrates of the Alkali and Alkaline Earth Metals. WILLIAM D. HARKINS and GEORGE L. CLARK (*J. Amer. Chem. Soc.*, 1915, **37**, 1816—1828).—The paper deals with the freezing points of: (1) mixtures in the complete system barium, sodium, and potassium nitrates; (2) mixtures in the neighbourhood of the eutectic point of the system strontium, sodium, and potassium nitrates; and (3) mixtures of barium, lithium, and potassium nitrates as far as the limits of stability. The apparatus and methods of plotting curves were similar to those adopted by Menzies and Dutt in the case of calcium, sodium, and potassium nitrates (A., 1911, ii, 882).

The melting point of barium nitrate is given as 595·53°. The eutectic point for the system $Ca(NO_3)_2$–KNO_3–$NaNO_3$ is 175° (*ibid.*); for the system $Sr(NO_3)_2$–KNO_3–$NaNO_3$ it is 208·4° (nine equivalents of $Sr(NO_3)_2$ to fifty of KNO_3 to forty-one of $NaNO_3$); and for the system $Ba(NO_3)_2$–KNO_3–$NaNO_3$ it is 214·1° (ratio, 5 : 50 : 45).

The determination of the liquidus surface for the system $LiNO_3$–KNO_3–$Ba(NO_3)_2$ was very much limited by the factor of stability. All points along the lines $Ba(NO_3)_2$–KNO_3 and $LiNO_3$–KNO_3 could be found, and it was possible to reach a point represented by a mixture of forty equivalents of $Ba(NO_3)_2$ to sixty of $LiNO_3$ (m .p. 436·6°) before decomposition was marked. Any ternary mixture containing as much as 10% of $Ba(NO_3)_2$, however, decomposed vigorously, even before it melted. The melting point of lithium nitrate is given as 254·1°, and the eutectic mixture of $LiNO_3$ and $Ba(NO_3)_2$ contains about 1 equivalent % of the latter. J. C. W.

Borates. The System $(NH_4)_2O$–B_2O_3–H_2O at 60°. III. U. SBORGI and F. MECACCI (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 1225—1231. Compare A., 1913, ii, 213, 318).—At 60° this system gives a continuous diagram, the compounds stable at this temperature being: $(NH_4)_2O,5B_2O_3,8H_2O$, which was obtained also at 30°; $(NH_4)_2O,4B_2O_3,6H_2O$, of which no analogue exists at 30°; and $(NH_4)_2O,2B_2O_3,4H_2O$. Each of these compounds is capable of existing unchanged in presence of pure water at 60°, the solubilities, calculated in parts of anhydrous salt per 100 parts of water, being 23·25, 33·79, and 41·81 for the 1—5, 1—4, and 1—2 compounds respectively. T. H. P.

The Chapter "Borax and Metallic Borates" in Analytical Text-books. L. VANINO (*Zeitsch. anal. Chem.*, 1915, **54**, 408—409).—The reaction between borax and soluble metallic salts is generally explained by the formation of borates, metaborates, pyroborates, etc., and gives rise to much confusion.

The reactions are best explained by the hydrolysis of the compounds. For instance, when mixing strong solutions of borax and barium chloride, BaB_4O_7 is obtained; with three extra molecules of water, two molecules of boric acid are liberated, and $Ba(BO_2)_2$ is formed; the latter with an extra four molecules of water yields a clear solution containing both barium hydroxide and free boric acid.

With silver nitrate, a similar reaction takes place, but the finally formed silver oxide remains undissolved. L. DE K.

Calcium Amalgams. L. CAMBI and G. SPERONI (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 599—605. Compare this vol., ii, 453, 670).—The authors have carried out a thermal analysis of these amalgams, which were prepared by a modification of Moissan and Chavanne's method (A., 1905, ii, 163). Amalgams with fewer than 33 atom. % of calcium contain the compound $CaHg_4$, m. p. 266° (decomp.). At higher temperatures, primary separation of the compound $CaHg_2$ probably occurs. Mixtures containing more than 14 atom. % of calcium do not melt completely at the ordinary pressure, but boil at 377°. No confirmation is obtained of the existence of compounds containing higher proportions of mercury than the above (compare Férée, A., 1899, ii, 155; Schürger, A., 1901, ii, 97; Moissan and Chavanne, *loc. cit.*).

Smith's results (this vol., ii, 89), although constituting an indirect proof of the existence of calcium mercurides in solution, furnish no direct information concerning the compounds separating in the solid state. T. H. P.

Use of Phosphorescent Calcium Sulphide in the Bacchanalian Rites. W. P. JORISSEN and J. H. WIETEN (*Chem. Weekblad*, 1915, **12**, 768—773).—A historical account of the part played by calcium sulphide in the worship of Bacchus. A. J. W.

The Phototropy of Inorganic Systems. System of Calcium Sulphide. JOSÉ RODRIGUEZ MOURELO (*Compt. rend.*, 1915, **161**, 172—175. Compare this vol., ii, 78).—Samples of calcium sulphide were prepared by heating together 100 grams of calcium carbonate, 0·1 gram of sodium chloride, 0·03 gram of sodium carbonate, flowers of sulphur, and the necessary active manganese compounds in amounts varying from 0·1 to 0·0001% of manganese to the calcium carbonate taken. The temperature of heating was from 300° to 1000°, and the time four hours. All the specimens thus prepared showed marked phototropy, but no phosphorescence. Under the influence of light, the colours assumed were shades of red or violet, and in one case a shade of yellow. The phototropy very quickly assumed its maximum intensity under the influence of light. The intensity of the phototropy increased as the percentage of phosphorogen diminished from 0·1 to 0·0001, but beyond this it decreased, and soon disappeared.

A second series, in which a second phosphorogen, namely, bismuth, was introduced gave the same results, the systems in this

case, however, being more sensitive to light, but the presence of the bismuth appeared to be without influence on the colours assumed. W. G.

Magnesium Ammonium Sulphate (Cerbolite). I and II. Solubility, Ice Curve, and Cryohydric Point. C. PORLEZZA (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 509—513, 596—599).—Divergent results having been obtained as regards the solubility of magnesium ammonium sulphate or cerbolite (compare Tobler, *Annalen*, 1855, **95**, 193; Mulder, *Scheikunde Verhandel.*, Rotterdam, 1864, 226; Locke, A., 1902, ii, 497; Lothian, A., 1910, ii, 504; Seidell, A., 1912, ii, 161), which is obtained as a bye-product in the Tuscan boric acid industry, the author has reinvestigated the question.

The cryohydric points, determined by the intersection of the ice curve and the solubility curve, are as follows: Seidell, $-1{\cdot}90°$; Lothian, $-2{\cdot}45°$; and the author, $-2{\cdot}40°$, the experimental value being $-2{\cdot}34°$; the concentration corresponding with the cryohydric temperature, determined from the graphic representation, is 10·75 grams of the anhydrous sulphate, $Mg(NH_4)_2(SO_4)_2$, per 100 grams of water. The equation $S=10{\cdot}55+0{\cdot}2215t+0{\cdot}000668t^2$ gives the solubility of the anhydrous sulphate per 100 grams of solution between 0° and 100° to within 1%. In all the solubility measurements, the solid phase was found to consist of

$$Mg(NH_4)_2(SO_4)_2,6H_2O,$$

so that no transformation point exists within the above limits of temperature. T. H. P.

Some Appliances for Metallographic Research. WALTER ROSENHAIN (*J. Inst. Metals*, 1915, **13**, 160—192).—Three appliances are described. The first is a levelling device for metal specimens, by means of which either the whole surface or any desired part of it may be set normally to the optical axis of the microscope. The usual mounting slip is used, placed on a level base of plate-glass, and the specimen is moved until the cross-wires of a vertical telescope and their reflected image coincide.

It has not been found practicable to obtain a rectilinear cooling curve from an electric furnace by varying the resistance in the heating circuit. The plan is therefore adopted of establishing a uniform temperature gradient within the furnace, and causing the specimen under examination to travel through the furnace at a uniform rate. The cylindrical furnace is placed vertically, and is only wound for the upper fifth of its length. The specimen and thermocouple are lowered through the tube by a motor provided with a centrifugal or liquid frictional governing device. The cold junction, a vacuum flask containing ice, travels down with the specimen, which may be enclosed in a silica tube when an inert atmosphere is required. The cooling curve of a substance without critical points is obtained as a straight line.

The third appliance is a chronograph for plotting inverse-rate curves. The instrument depends on the movement of a pen at a regular rate over paper on a rotating drum. The observer taps a

key when the galvanometer needle or spot crosses a division of the scale, and thus marks the paper. The pen at once returns to zero, whilst the drum is turned through a small angle, and the pen again starts to travel along the length of the drum at the same uniform rate. The actual construction is complicated. Critical points on cooling curves are very clearly indicated. C. H. D.

Etching Reagents and their Application. O. F. HUDSON (*J. Inst. Metals*, 1915, **13**, 193—221).—A review of the reagents suitable for developing the structure of metallic alloys. Polish attack with dilute ammonia on parchment is recommended for brasses. Alloys of copper and nickel are not readily etched by the ordinary reagents, and electrolytic etching in dilute sulphuric acid containing hydrogen peroxide gives the best results. C. H. D.

Copper–Aluminium Alloys. J. H. ANDREW (*J. Inst. Metals*, 1915, **13**, 249—262).—The temperature of the $\alpha\delta$-eutectoid transformation is probably 545°. The position of the line separating the γ- and δ-regions has also been determined. The development of heat at 290° during the cooling of alloys containing from 9 to 16% of aluminium is attributed to the undercooling of the β-constituent. C. H. D.

The Micro-chemistry of Corrosion. III. The $\alpha\beta$-Alloys of Copper and Zinc. SAMUEL WHYTE (*J. Inst. Metals*, 1915, **13**, 80—99. Compare Desch and Whyte, A., 1914, ii, 367, 655).—The behaviour of alloys of the Muntz metal class, containing about 60% of copper, has been examined by means of an improved form of electrolytic apparatus. The total conversion under given conditions is less than that of the β-, but greater than that of the α-, alloys. Corrosion takes place by dezincification of the β-constituent, and then spreads to the α-constituent, a spongy mass of copper remaining. Annealing diminishes the rate of corrosion and the relative dezincification. Corrosion is accelerated by the presence of 1% of iron or lead, the adherent layer of basic salts being in both cases open in texture, whilst 1% of tin leads to the formation of a firmly adherent white layer, which retards corrosion.

A comparison with corroded bolts and condenser tubes which have been exposed to sea-water shows that natural and electrically stimulated corrosion follow the same course. C. H. D.

The Quantitative Effect of Rapid Cooling on the Constitution of Binary Alloys. III. G. H. GULLIVER (*J. Inst. Metals*, 1915, **13**, 263—291).—The mathematical treatment previously described (A., 1914, ii, 623) is applied to the series lead-tin, copper-tin, copper-zinc, copper-nickel, and copper-aluminium, the form of the apparent solidus curve being calculated for different rates of cooling in each case. C. H. D.

The Constitution of the Alloys of Copper with Tin. I. and II. JOHN L. HAUGHTON (*J. Inst. Metals*, 1915, **13**, 222—248. Compare Heycock and Neville, A., 1904, ii, 172; Giolitti and Tavanti, A., 1908, ii, 946).—The alloys at the tin end of the

series have been investigated. Rapid cooling from the molten state is obtained by casting into a wedge-shaped mould of thin sheet copper immersed in a freezing mixture. Heating curves are taken, and annealing experiments made at different temperatures. More accurate indications are obtained from heating than from cooling curves. The boundary between the η- and ϵ-regions has been fixed, the temperature of transformation being 401° on cooling and 415° on heating. C. H. D.

Constitution of Ultramarine. Paul Rohland (*Kolloid. Zeitsch.*, 1915, **16**, 145—146).—It is suggested that the various ultramarines are adsorption compounds in which colloidal sulphur (or sulphur compounds) has been adsorbed by colloidal silicates. H. M. D.

Alloys of Manganese and Gold. N. Parravano (*Gazzetta*, 1915, **45**, i, 293—303).—The solidification diagram of these alloys has been investigated, oxidation being prevented by means of a current of hydrogen.

Manganese dissolves in the solid state in gold in proportions up to 10·5%, and gold in manganese up to about 25%. The fusion diagram is more complicated than any given in Tammann's scheme. A sharp maximum occurs at the composition AuMn, this compound being capable of dissolving either gold or manganese in the solid state. A liquid miscibility gap occurs between 50% and 57·5% of manganese, and certain complex transformations, the nature of which has not been determined, take place in the solid state. Manganese thus differs markedly in behaviour from iron, cobalt, and nickel, and gold from its homologue, copper.

The hardness curve exhibits a minimum in exact correspondence with the maximum of the fusion curve. Micrographic studies of the different alloys were also made. T. H. P.

The Passivity of Iron. A. Smits (*Chem. Weekblad*, 1915, **12**, 676—694).—A theoretical paper, summarising the work done on the passivity of iron, and discussing the results obtained. A. J. W.

The Influence of Phosphorus on the Properties of Grey Cast Iron. F. Wüst and R. Stotz (*Ferrum*, 1915, **12**, 89—96, 105—119).—Cast irons containing 3·3% of carbon, the graphite varying from 1·80 to 2·92%, and phosphorus from 0·03 to 2·04%, have been investigated. The tensile and bending strengths are increased by phosphorus up to 0·3%, whilst from 0·6% upwards the strength diminishes with increasing phosphorus. The resistance to shock diminishes with increasing phosphorus up to 0·6%, and after that only very slightly. The hardness increases nearly in proportion to the phosphorus content.

The influence of phosphorus is nearly independent of the quantity of other elements present. Manganese does not intensify the harmful effect.

The microscopic structure is considerably affected. With in-

creasing phosphorus, the graphite tends to form granular masses rather than plates, the ternary eutectic makes its appearance, and uniform pearlite is replaced by masses of lamellar pearlite and fine sorbite. The presence of manganese causes a finer structure in the pearlite. C. H. D.

Iron Carbides and their Catalytic Influence on the Decomposition of Carbon Monoxide. SIEGFRIED HILPERT and THEODOR DIECKMANN (*Ber.*, 1915, **48**, 1281—1286).—The influence of contact with solid matter, such as metals and metallic oxides, or the dissociation of carbon monoxide into carbon dioxide and carbon, needs further investigation (compare Schenk and Zimmermann, A., 1903, ii, 423). The authors have therefore examined the effect produced by pure iron oxide, and the various reaction products to which it gives rise.

At 950°, iron oxide is reduced by carbon monoxide to metallic iron, although at this temperature the gas has little tendency to liberate carbon; at and below 850°, however, iron is converted into the carbide, and deposition of the carbon also occurs rapidly after the content of carbon in the contact material has reached 6%. It thus appears that it is not metallic iron, but the carbide, Fe_3C, which catalyses the dissociation of the carbon monoxide, and this view is confirmed by the fact that the Curie point at which the solid phase on which carbon has deposited loses its magnetic properties is 183°, whereas for pure iron it is 700°, and for cementite it is 235°. The conclusion is therefore drawn that the mechanism of the action of the carbide involves the formation of unstable higher carbides, which again decompose into Fe_3C and carbon, the behaviour towards hydrochloric acid of the black solid products obtained being held to accord with this view.

The presence of arsenic does not affect the catalytic activity of the iron carbide. D. F. T.

The Properties of some Nickel-Aluminium and Copper-Nickel-Aluminium Alloys. A. A. READ and R. H. GREAVES (*J. Inst. Metals*, 1915, **13**, 100—159).—The melting points of the light aluminium alloys are lowered by the addition of either copper or nickel, and the results point to the formation of a ternary eutectic. The specific gravity is a linear function of the sum of the copper and nickel present. The nickel has no favourable effect on the mechanical properties, and increases the liability to corrosion.

C. H. D.

Recovery of Ammonium Molybdate used in Phosphate Estimations. J. A. PRESCOTT (*Analyst*, 1915, **40**, 390—391).—The residues, such as the filtrates from phosphomolybdate precipitates, solutions of the latter in ammonia, and ignited residues, are evaporated. A syrupy liquid is obtained, from which phosphomolybdate and molybdic acid have separated mixed with crystals of ammonium sulphate and nitrate. The precipitate is collected, washed with cold water, then dissolved in ammonia, and the solution treated with magnesia mixture to precipitate the phosphoric

acid. After filtration, the solution is evaporated to a small volume, and the ammonium molybdate allowed to crystallise; the mother liquors are worked up with subsequent quantities of residues. A blue solution is sometimes obtained when the molybdic acid is dissolved in ammonia; in such cases, a quantity of hydrogen peroxide must be added to oxidise the lower molybdenum oxides.

W. P. S.

Nickelomolybdates. G. A. Barbieri (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 357—362).—The composition of the nickelomolybdates prepared by Hall (A., 1907, ii, 555) are in accord, not with the formulæ given by this author, but with

$$2(NH_4)_2O,NiO,6MoO_3,8H_2O$$

and $2K_2O,NiO,6MoO_3,8H_2O$. A number of other nickelomolybdates have also been prepared. In the guanidine salt, nickelomolybdic acid is sexavalent, and since also they give up the final $3H_2O$ only slowly at above 155°, the nickelomolybdates are regarded as acid salts of a decabasic hetero-poly-acid. The following salts were prepared and analysed.

Ammonium, $(NH_4)_4H_6[Ni(MoO_4)_6],5H_2O$, blue, microscopic scales; *potassium*, of similar form, and only becoming anhydrous at about 350°; *barium*, $Ba_2H_6[Ni(MoO_4)_6],10H_2O$; *silver*, $(+3H_2O)$; and *guanidine*, $(CH_6N_3)_6H_4[Ni(MoO_4)_6],7H_2O$.

T. H. P.

Bismuth Suboxide. W. Herz (*Zeitsch. anal. Chem.*, 1915, **54**, 413).—Polemical. A reply to Treubert and Vanino (this vol., ii, 471) as to the existence of bismuth suboxide. L. de K.

I. Sodium Columbates. II. Atomic Weight of Columbium. Edgar F. Smith and Walter K. van Haagen (*J. Amer. Chem. Soc.*, 1915, **37**, 1783—1797).—I. *Sodium Columbates.*—The only sodium columbates which can be regarded as definite individuals are the salt, $7Na_2O,6Cb_2O_5,31H_2O$, described by Bedford (A., 1905, ii, 832), and the metacolumbate, $Na_2O,Cb_2O_5,7H_2O$, of Balke and Smith (A., 1908, ii, 1044). It was thought that the latter salt would afford an entirely new means of determining the atomic weight of columbium, and therefore experiments were undertaken in order to make sure whether it could be prepared really pure. The former (7 : 6) salt was obtained by adding a large excess of sodium hydroxide to a solution of potassium oxyfluocolumbate, washing the heavy precipitate of the sodium columbate a few times with cold water, and crystallising it from boiling water. The mother liquors gave the 1 : 1 salt on spontaneous evaporation, the change being due to hydrolysis, thus: $7Na_2O,6Cb_2O_5 + H_2O = 6(Na_2O,Cb_2O_5) + 2NaOH$. On adding alcohol slowly to a solution of the latter salt, however, the 7 : 6 salt gradually separated, according to the equation

$$7(Na_2O,Cb_2O_5) = 7Na_2O,6Cb_2O_5 + Cb_2O_5,$$

the columbic acid, or more probably an acid columbate, remaining in solution. This shows that the two salts are mutually con-

vertible, and suggests that the preparation of the 1:1 salt from the 7:6 might be expedited by the use of carbon dioxide. A current of the gas passing through the solution caused the hydrolysis to proceed too far, but when the solution was slowly evaporated on the water-bath in an atmosphere of carbon dioxide, an excellent yield of the desired salt was obtained. However, the metacolumbate will not suffer recrystallisation, but it was found that the first well-washed crystals were perfectly pure.

II. *Atomic Weight of Columbium.*—The new determination depended on the estimation of the ratio $NaCbO_3$:NaCl, which was effected by the action of sulphur chloride on the above dehydrated sodium metacolumbate. The latter salt was prepared from potassium fluocolumbate (*ibid.*), dehydrated at 800°, and then a weighed portion was heated in a current of sulphur chloride vapour. It was found that the last traces of columbium did not volatilise until the mass had been moistened with water, dried again, and re-heated in the stream of sulphur chloride. On the other hand, the residual sodium chloride was free from sulphur. Details of the special apparatus and of the manipulation are given. As a mean of seven determinations with two samples of the sodium columbate, the value 93·13 is deduced for the atomic weight of columbium. J. C. W.

Analysis of some Ural Platinums. Ide Koifman (*Arch. Sci. phys. nat.*, 1915, [iv], **40**, 22—38).—The following are the average percentage results obtained in the analyses of specimens of the metal from various mines in the Ural district:

	Taguil.	Iss.	Omoutnaya.	Kitlim.	Iow.	Kamenoutchka.
Os ...	1·44	4·47	10·88	0·79	20·13	4·98
Pt ...	77·55	85·10	77·61	83·50	60·53	82·46
Ir ...	2·56	1·38	6·39	2·74	6·72	1·79
Rh ...	0·52	0·30	0·43	0·62	0·74	0·69
Pd ...	0·26	0·30	0·32	0·28	0·19	0·18
Cu ...	3·27	0·63	1·95	1·14	0·52	0·54
Fe ...	14·46	7·86	2·60	11·05	11·38	9·49

The methods used for separating the metals are described. W. P. S.

Mineralogical Chemistry.

Exhalations from Etna. I. and II. G. Ponte (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 341—347, 402—408).—According to Deville (*Compt. rend.*, 1856, **43**, 955), (1) the nature of the fumaroles of an active volcano at any given time varies with the distance from the eruptive centre, and (2) the nature of the exhalations from an active volcano at a definite place varies from the beginning to the end of the eruption. The author's analyses of the gases

evolved during the lateral eruption of Etna in 1911 confirm the second of the above laws, and indicate that the variations in the composition of the gas are influenced by the temperature and by atmospheric agents. Brun (A., 1907, ii, 33) has stated that a knowledge of the various temperatures in a volcano is sufficient to characterise clearly the state of activity, since all volcanoes emit the same gases at a definite temperature, whether the magma is acid or basic in character. The author points out that this would hold only when the gases were emitted either into a vacuum or into the external air under definite conditions, since marked reactions may be produced in the gases by atmospheric agencies.

The proportion of ferrous oxide in lava is influenced, not only by prolonged exposure in a pulverulent condition, but also by the duration of its heating in contact with the air. Highly porous, superficial layers of lava contain considerably less ferrous oxide than compact lava, and hot fumaroles, emitting only water vapour with a neutral reaction, exhibit an internal red stratum of oxide of iron. Experiment shows that water vapour and air exert an energetic oxidising action on red-hot lava. T. H. P.

Bournonite from Park City, Utah. Frank R. Van Horn and W. F. Hunt (*Amer. J. Sci.*, 1915, [iv], **40**, 145—150).—A description is given of three large crystals of bournonite from the Silver King mine. Analysis, by W. R. Veazey, of material from the Daly West mine, agrees closely with the usual formula, $PbCuSbS_3$.

Pb.	Cu.	Sb.	S.	Total.	Sp. gr.
43·18	13·14	25·03	19·59	100·94	5·829

L. J. S.

Manganiferous Albite from California. E. H. Kraus and W. F. Hunt (*Centr. Min.*, 1915, 465—467).—Black (anal. I, D 2·688) and yellow (anal. II) albites with a platy structure have been found in the Carterina mine, Heriart Mountain, near Pala, in California. Analysis I corresponds with 90·7% albite and 9·3% anorthite. The colour is due to microscopic enclosures of iron and manganese oxides.

	SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
I.	64·44	20·28	0·98	1·71	1·76	0·11	9·83	0·49	0·96	100·56
II.	64·12	20·83	1·07	trace	1·97	—	—	—	—	—

L. J. S.

The Crystallisation of Haplobasaltic, Haplodioritic, and Related Magmas. N. L. Bowen (*Amer. J. Sci.*, 1915, [iv], **40**, 161—185).—The ternary system diopside–anorthite–albite has been studied in detail by the quenching method (A., 1913, ii, 613), and the results are given in a series of equilibrium diagrams. These fusions correspond with simple magmas consisting of a mixture of diopside with a plagioclase—those with labradorite being called haplobasaltic, those with andesine haplodioritic, etc.

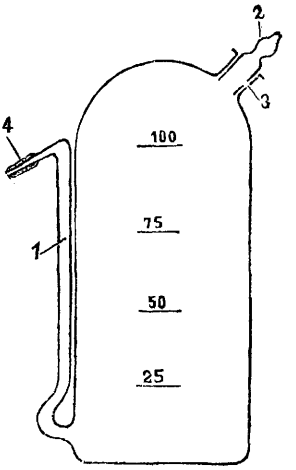
L. J. S.

Analytical Chemistry.

Modified Burette-calibrating Pipette and Certain Points in the Use of such Instruments. C. W. FOULK (*J. Ind. Eng. Chem.*, 1915. **7**, 689—693).—The pipette described is provided with a two-way tap at its lower end; in one position, this tap connects the pipette through a side-tube with the burette to be calibrated, and in the other position it allows the contents of the pipette to be discharged. A mark is placed on the upper stem of the pipette, whilst the tap forms the zero point. The capacity of the pipette itself is determined previous to use by weighing the quantity of water required to fill it. A discussion of the principles underlying the calibration and use of such pipettes is also given.

W. P. S.

A New Weighing Burette. GEORG INCZE (*Zeitsch. anal. Chem.*, 1915, **54**, 406—408).—The apparatus (see Fig.), which weighs about 40 grams, consists of a vessel of about 100 c.c. capacity with a narrow delivery tube, 1. The burette is filled with the standard solution through the aperture of the stopper, 2. This stopper is well ground, and by means of a hole bored through stopper and tubulus serves to regulate the entrance of the air, and hence the size of the drops. The liquid will only flow out when the burette is appropriately inclined, and is delivered at will either in drops or in a jet. The end 4 of the dropping tube, and this is highly important, is covered with a coating of beeswax.



The burette is weighed before and after delivering the liquid. The author urges that the results found by weight must be far superior to those found by measurement from an ordinary burette, all the drawbacks of the latter being avoided. The burette is furnished with a rough scale to give an idea as to the c.c.'s of solution used. When using this burette, all volumetric solutions should be made up to a definite weight instead of volume.

L. DE K.

Extraction by Immiscible Solvents. P. A. W. SELF (*Pharm. J.*, 1915, **95**, 164—165).—A review of the advantages and disadvantages of immiscible solvents in common use, and of the methods of avoiding emulsification during extraction. Chloroform emulsifies more readily than ethyl ether or light petroleum,

but has the advantage usually of giving a purer product, in addition to the fact that no alcohol or water remains in the evaporated extract. It is particularly suitable for alkaloids and aromatic substances. Light petroleum is recommended for the extraction of fats and volatile oils, whilst benzene may often be substituted for chloroform for extracting aromatic substances. For the avoidance of emulsification, the author particularly recommends the use of a comparatively large volume of solvent, and examples are given where complete separation was obtained with large volumes of solvent (two to five times the volume of the liquid to be extracted) where an inseparable emulsion was formed under similar conditions, using small quantities of solvent. The use of mixed solvents, or of two solvents in succession, the addition, where practicable, of various substances (mineral acids or alcohol), to the liquid to be extracted, or the previous removal of substances, such as fats, which cause the emulsification, are available, but generally less successful, methods for avoiding the formation of an emulsion. For breaking down an emulsion already formed, shaking with more of the solvent is, in the author's opinion, more efficacious than either warming, filtering under pressure, or centrifuging. G. F. M.

Acidimetric itrations with Phenolphthalein. ANNIBALE FERRARO (*Boll. chim. farm.*, 1915, **54**, 257—258).—When flour, etc., is lixiviated with water, and the extract titrated with alkali solution in presence of phenolphthalein, the red coloration persists for some time, whereas with extracts obtained by lixiviation with neutral 90% alcohol, the red colour obtained on titration rapidly diminishes in intensity, or disappears entirely. The alkali salt appears to be more stable in water than in alcohol, and addition of water to the latter restores the coloration, which is then more intense than at first. In order to avoid error in the titration of these alcoholic extracts, it is advisable to dilute them with about the twofold volume of water before titration. T. H. P.

A New Reaction for Hydrogen Peroxide. K. SPIRO (*Zeitsch. anal. Chem.*, 1915, **54**, 345—347).—If to a dilute solution of phenol is added a few drops of a dilute ($N/10$) solution of hydrogen peroxide, and then a little freshly prepared $N/100$-ferrous sulphate solution, an emerald-green, preceded by a bluish-violet, colour is developed. If now is added a little weak alkali (ammonia, ammonium carbonate, or sodium carbonate), the green colour turns to reddish-violet, which, on adding acid, again turns green. In place of phenol, other monohydroxyl derivatives of benzene may be used, such as cresol, *p*-hydroxybenzoic acid, tyrosine, picric acid, etc.; also salicylaldehyde, but not salicylic acid. The reaction is caused by the oxidising power of the hydrogen peroxide, both on the phenol and the iron. The reaction fails, of course, in the presence of salts which form complex iron compounds, such as tartrates or cyanides. L. DE K.

Experimental Data Comparing the Sensitiveness of Different Tests for Hydrogen Peroxide in Milk. IRWIN T. DARLINGTON (*J. Ind. Eng. Chem.*, 1915, **7**, 676).—Comparative tests showed that *p*-phenylenediamine is the most sensitive reagent for the detection of hydrogen peroxide in milk; it will detect the presence of 0·00075 gram of hydrogen peroxide per 100 c.c. Benzidine is almost as sensitive, but potassium iodide and starch, titanic acid, and vanadic acid reagents do not yield a positive reaction when the quantity of peroxide is less than 0·003 gram per 100 c.c. Attention is drawn to the fact that hydrogen peroxide is reduced rapidly by milk, and that the quantity which would be added to milk as a preservative disappears entirely within eighteen hours, the milk then no longer giving a reaction. W. P. S.

Estimation of Ash in Bread. K. SCHERINGA (*Chem. Weekblad*, 1915, **12**, 702—703).—A criticism of the work of Filippo and Adriani (this vol., ii, 604), and a description of a modified method for estimating ash in bread. A. J. W.

Estimation of Chlorine in Foodstuffs containing Sodium Chloride. J. D. FILIPPO and W. ADRIANI (*Chem. Weekblad*, 1915, **12**, 703—706).—A reply to Scheringa, and an account of further results obtained by the authors' method. A. J. W.

Estimation of Ash in Bread containing Sodium Chloride. C. K. ZYLSTRA (*Chem. Weekblad*, 1915, **12**, 745—748).—The author describes experimental results supporting the work of Filippo and Adriani (this vol., ii, 604). A. J. W.

Estimation of Chlorine in Bread. K. SCHERINGA (*Chem. Weekblad*, 1915, **12**, 749—751).—An account of further results obtained by the author's method of estimating the chlorides present in bread-ash. A. J. W.

Estimation of Chlorine in Bread. J. D. FILIPPO and W. ADRIANI (*Chem. Weekblad*, 1915, **12**, 805—807).—A description of further determinations of the amount of chlorides in bread by the authors' method. A. J. W.

Recent Methods for the Estimation of Total Sulphur in Rubber. J. B. TUTTLE and A. ISAACS (*J. Ind. Eng. Chem.*, 1915, **7**, 658—663).—Methods which depend on the oxidation of the sulphur by heating with nitric acid or by fusion with sodium peroxide, potassium nitrate, etc., are found to yield untrustworthy results; loss of sulphur occurs in the direct fusion methods, and the loss increases with the sulphur content of the caoutchouc. A method described previously by Waters and Tuttle is recommended for the purpose. In this method, the caoutchouc is treated for one hour in a covered porcelain crucible with 25 c.c. of nitric acid saturated with bromine, then heated for one hour on a water-bath, and evaporated to dryness after removing the cover. The

residue is fused with 5 grams of fusion mixture, cooled, extracted with hot water, the solution filtered, and the sulphate estimated gravimetrically. It is suggested that the free sulphur and the sulphur remaining after extraction with acetone should be estimated separately, the sum of the two quantities giving the amount of total sulphur. This procedure eliminates the troublesome effect of the free sulphur on the estimation of the total sulphur.

W. P. S.

Estimation of Sulphates in Soils. P. E. Brown and E. H. Kellogg (*J. Ind. Eng. Chem.*, 1915, **7**, 686—687).—Sulphates cannot be extracted completely from soils by treatment with dilute hydrochloric acid, because organic substances and iron compounds interfere; when more concentrated hydrochloric acid is used, silica is also dissolved, and interferes with the estimation of the sulphate. Trustworthy results may, however, be obtained by shaking the soil for eight hours with twice its weight of water; under these conditions, the soluble sulphates, including calcium sulphate, are extracted completely. The use of the sulphur-photometer is recommended for the estimation of sulphates. W. P. S.

Kjeldahl Distillation Apparatus. Arthur D. Holmes (*J. Ind. Eng. Chem.*, 1915, **7**, 693—694).—The height of the distillation apparatus described previously by the author (this vol., ii, 65) may be decreased 6 or 8 inches by using a horizontal burner and shortening the condenser accordingly. W. P. S.

[Estimation of Ammonia in Plants.] Ciro Ravenna (*Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 302—306).—Compare this vol., i, 925.

Estimation of Phosphorus Hydride. II. Volumetric Methods. H. Reckleben (*Zeitsch. anal. Chem.*, 1915, **54**, 308—321. Compare this vol., ii, 483).—The author states that the gravimetric methods usually employed, and also the processes involving the titration of the excess of the reagent added, do not give satisfactory results. Approximate results may be calculated from the weight of the precipitates obtained by means of ammoniacal silver nitrate or alkaline copper tartrate (Ag and Cu_2O respectively).

Accurate results are obtained by the use of excess of chlorine or bromine water; the phosphoric acid may then be determined gravimetrically, say, by the molybdate process.

A solution of potassium permanganate is also serviceable; the excess of permanganate may be titrated as usual, and the liquid then tested for phosphoric acid with ammonium molybdate.

L. de K.

Nephelometric Estimation of Small Quantities of Phosphoric Acid. H. Serger (*Chem. Zeit*, 1915, **39**, 613).—Twenty-five c.c. of molybdic acid reagent, 20 c.c. of concentrated nitric acid, and 5 c.c. of the phosphoric acid solution (acidified with nitric acid) are heated at 70° in a beaker 8 cm. high and 4 cm. in diameter; a mixture of 25 c.c. of molybdic acid reagent and

20 c.c. of concentrated nitric acid is treated similarly in another beaker. The two beakers are then placed on a black plate, and $N/500$-phosphoric acid solution (each c.c. is equivalent to 0·0000372 gram of P_2O_5) is added from a burette to the contents of the second beaker until the turbidity obtained corresponds with that exhibited by the contents of the first beaker. For the estimation of phosphoric acid in water, from 100 to 300 c.c. of the sample are evaporated in a platinum basin to dryness, the residue dissolved in 2·5 c.c. of nitric acid, the solution filtered, and the filter washed with 2·5 c.c. of nitric acid; the 5 c.c. of filtrate thus obtained are used for the estimation. W. P. S.

Identification and Estimation of Arsenic in Organic Combination. L. BARTHE (*Ann. Chim. anal.*, 1915, **20**, 175—178; from *Bull. Soc. pharm. Bordeaux*, 1914).—When the arsenic organic compound is not mixed with other organic substances, the arsenic may be precipitated as sulphide after the compound has been decomposed by heating with sulphuric acid. If other organic substances are present, it is necessary to oxidise the mixture by heating with sulphuric and nitric acids before the arsenic is separated as sulphide. Bougalt's reagent (hypophosphorous acid in hydrochloric acid solution) and Bressanin's reaction (formation of arsenic tri-iodide in hydrochloric acid solution), although useful in certain cases, will not distinguish arsenic from mercury compounds, etc. W. P. S.

The Estimation of Traces of Carbon Monoxide in the Atmosphere. ARMAND GAUTIER (*Bull. Soc. chim.*, 1915, [iv], **17**, 256—259. Compare A., 1898, ii, 535, 537, 640).—A claim for priority over Graham and Winmill (compare T., 1914, **105**, 1996) for the use of iodine pentoxide as oxidising agent in the estimation of traces of carbon monoxide in the atmosphere. W. G.

A Method of Collecting and Analysing Flue Gases and Industrial Gases. A Filter for Flue Gases. ARMAND GAUTIER (*Bull. Soc. chim.*, 1915, [iv], **17**, 273—278).—The collecting portion of the apparatus consists of an iron tube, long enough to go right across the flue, closed at one end, and having two longitudinal slits extending nearly the whole length of the tube. Inside this is a shorter nickel-iron tube, also closed at the inner end, and having a hole just opposite the central portion of the outer tube where it is not cut. This is put through a hole in the flue about 4 to 5 metres above the fire. After being cooled, the gases pass from this tube to a wash-bottle containing marbles and a little water, and from there to the filter proper, which consists of two wide platinum cones, clamped at their edges and having between them three ash-free, tared filter-papers. From these the gases pass to a gas-meter, and then on to the aspirator, which is used to maintain a steady flow of the gases through the apparatus. At the end of the experiment, the filter-papers are removed to a funnel, and the water containing the dust and tarry matter is filtered through them. The papers are

then dried at 100° and weighed, the inner paper serving as a tare to the one containing the deposit. By this method, the solid matter collected has been found to vary with coal from 0·80 to 0·006 gram per cub. metre of flue gas, and with coke it is about four times less. W. G.

[Acidimetric] Estimation of Hardness in Waters with Due Regard to the Presence of Alkali Carbonates. OTTO MAYER (*Zeitsch. anal. Chem.*, 1915, **54**, 289—308).—Magnesium carbonate is but incompletely precipitated on boiling. Some of it is mechanically carried down by the calcium carbonate deposit, and some of it may react with any calcium sulphate present, generating an additional quantity of calcium carbonate; anyhow, the alkalinity of the filtrate is due partly, or even entirely, to magnesium carbonate. True alkali carbonates may be detected by taking up the residue of some 50—100 c.c. of water with alcohol of D 0·805 containing a little phenolphthalein solution.

For the estimation of alkali carbonates, 1 litre of the sample is evaporated in a nickel dish nearly to dryness, and the residue extracted repeatedly with portions of 50 c.c. of the weak alcohol until the liquid no longer reacts with phenolphthalein. The united alcoholic filtrates are evaporated to expel the alcohol, and the aqueous fluid titrated with $N/10$-hydrochloric acid with methyl-orange as indicator. The result deducted from the alkalinity of the water = magnesium carbonate.

For a direct estimation of the temporary hardness, the precipitate formed on boiling, together with 10 c.c. of the filtrate (which is used for other purposes) is dissolved in $N/10$-acid, boiled, and titrated back with $N/10$-alkali. Allowance is then made for the alkalinity of the 10 c.c. filtrate, if any.

When determining the total hardness according to Wartha's method, the author prefers titrating the precipitate formed on boiling with the alkali mixture, instead of titrating the excess of alkali in the filtrate. As the precipitate must not be washed with water, the adhering alkali is removed by washing with 70% alcohol.

Boiling under high pressures yields deposits differing from the amount that would be expected from the permanent hardness found. L. DE K.

A Rapid Method for Estimating Calcium in Urine and Fæces. HENRY LYMAN (*J. Biol. Chem.*, 1915, **21**, 551—556).—The whole operation can be completed in twenty-five minutes, and consists of three main steps: (1) isolation of the calcium as oxalate; (2) solution of the oxalate in dilute acid; and (3) precipitation of the calcium as soap by potassium ricinate. The cloud formed is compared with that of a standard solution in a Duboscq colorimeter. W. D. H.

Modification of Meigen's Differential Reaction between Calcite and Aragonite. E. QUERCIGH (*Atti R. Accad. Lincei*, 1915, [v], **24**, i, 1231—1235).—Meigen's reaction for distinguishing

between calcite and aragonite (A., 1901, ii, 692; 1905, ii, 454) is effective only with colourless or feebly coloured minerals, and is inapplicable to mixtures of the two minerals. These inconveniences are overcome by converting the basic cobalt carbonate deposited on the mineral into the sulphide; aragonite then assumes a decidedly black coloration, whilst calcite changes but little, and becomes only slightly grey or ash-coloured. In mixtures of the two phases, the granules of the one are readily distinguishable from those of the other. The powder tested should be neither too fine nor coarser than 0·2—0·4 mm.; the concentration of the cobalt nitrate solution used should be 5% of the hexahydrated salt, and the boiling in an ordinary test-tube should last just half a minute; the sodium or ammonium sulphide solution may be of any reasonable strength. The sulphide may, in certain cases, replace the potassium chromate of Thugutt's test (A., 1911, ii, 334) with advantage. T. H. P.

Estimation of Lead as Sulphite. GEORGE S. JAMIESON (*Amer. J. Sci.*, 1915, [iv], **40**, 157—160).—The method depends on the insolubility of lead sulphite (compare A., 1914, ii, 386). The neutral or slightly acid lead solution is diluted to 100 c.c., and a small excess of 2% sodium hydrogen sulphite solution is added; after one hour, the precipitated lead sulphite is collected, washed with cold water, dried at 150°, and weighed. In cases where the lead solution contains free acid, the acidity is nearly neutralised with ammonia before the sodium hydrogen sulphite is added; the subsequent addition of sodium acetate is recommended when dealing with unknown quantities of lead and free acid. If copper is present, the precipitate of lead sulphite should be washed once by decantation, and then heated for five minutes with 15 c.c. of concentrated ammonium sulphite solution before it is collected for weighing. When the quantity of lead used for the estimation varies from 0·1 to 0·2 gram, the maximum error in the results obtained is ±0·004 gram. The method cannot be applied to the estimation of lead in the presence of calcium salts. W. P. S.

Method for the Estimation of Copper in Commercial Copper Sulphates. G. INCZE (*Zeitsch. anal. Chem.*, 1915, **54**, 412—413. Compare this vol., ii, 487).—The true reaction which takes place on adding a mixture of sodium thiosulphate and thiocyanate to a solution of copper sulphate is represented by the equations:

$$2CuSO_4 + 2Na_2S_2O_3 = Cu_2SO_4 + Na_2S_4O_6 + Na_2SO_4,$$
$$Cu_2SO_4 + 2NH_4CNS = 2CuCNS + (NH_4)_2SO_4.$$

L. DE K.

Estimation of Aluminium in Silicates. EMMERICH SELCH (*Zeitsch. anal. Chem.*, 1915, **54**, 395—403).—The well-known process of decomposing silicates by means of hydrofluoric and sulphuric acids gives good results if the last traces of fluorine are expelled by a second evaporation with dilute sulphuric acid (1:5), finally increasing the heat to expel the acid.

When using the alkali fusion, the weighed silica obtained should be examined for alumina by evaporating with hydrofluoric and sulphuric acid, finally igniting in a covered crucible over the blow-pipe.

The alumina obtained should also be submitted to the same treatment, the loss being recorded as silica. L. DE K.

Estimation of Ferrous Iron in Silicates by Titration with Dichromate. O. L. BARNEBEY (*J. Amer. Chem. Soc.*, 1915, **37**, 1829—1835).—The solution of the silicate, containing hydrofluoric acid, may also be titrated by the dichromate method if boric acid is added to counteract the hydrofluoric acid (compare this vol., ii, 583).

The author has frequently observed that the sensitiveness of the ferricyanide reaction for ferrous iron is greatly influenced by the strength of the hydrochloric acid in the solution. Numerous experiments are now described which illustrate this influence, and it is recommended that when small amounts of iron are to be titrated by the dichromate method, there should not be more than 5 c.c. of concentrated hydrochloric acid present in 200 c.c. of solution. If the concentration is larger, ferric chloride should be added to give a sharper test on the spot plate. J. C. W.

Separation of Platinum from Solutions of Ores previous to the Volumetric Estimation of Iron in the Same. L. BRANDT (*Chem. Zeit.*, 1915, **39**, 553—555).—The small quantities of platinum which pass into solution when iron ores are fused or dissolved in platinum vessels may be precipitated by treating the hot solution with stannous chloride and arsenious acid solutions; the platinum thus separated is removed by filtration, and the iron is estimated by the dichromate titration method, using diphenylcarbohydrazide as the indicator (A., 1914, ii, 71). Separation of the platinum by reduction with magnesium does not always yield trustworthy results, especially if the ore has been fused with alkali carbonates. W. P. S.

Method of Control Permitting of the Rapid Estimation of the Amount of Nickel Deposited on Nickel-plated Articles. M. PONTIO (*Compt. rend.*, 1915, **161**, 175—177).—The reagent employed is prepared by mixing water 50 c.c., nitric acid (D 1·3325) 10 c.c., hydrochloric acid (D 1·18) 20 c.c., and hydrogen peroxide (12 vol.) 20 c.c., and the procedure is as follows. One drop of the reagent is placed on the article to be examined, and left in contact for two minutes, and then one drop of dilute ammonia is added. After one minute, the liquid is poured on to a porcelain plate, and should not be coloured blue if the article being plated was of copper, or yellow or brown if the article was of iron. The copper can be further tested for by the addition of one drop of potassium ferrocyanide to the liquid on the white plate. This length of time of contact corresponds with a deposit of 1 mg. of nickel per sq. cm. in the case of copper articles and

4 mg. in the case of iron. By this method other periods of contact could be established for other thicknesses of nickel deposit. The same method could be employed for controlling the deposit of silver on copper or brass. W. G.

Detection of Various Mineral and Alkaloidal Poisons in Waters. Pierre Breteau (*J. Pharm. Chim.*, 1915, [vii], **12**, 68—73).—Five hundred c.c. of the water are rendered alkaline with sodium carbonate, and shaken with 20 c.c. of chloroform; the latter is separated, evaporated, and if any residue is obtained, portions of it are tested with general alkaloidal reagents. Should indications be obtained of the presence of alkaloids, other portions of the residue are tested with specific reagents for the identification of the alkaloid present. The water separated from the chloroform is then acidified with acetic acid, a small quantity of ferric chloride is added, followed by ammonia, until a precipitate of ferric hydroxide is obtained; the latter will contain any arsenic or antimony which may be present, and these may be identified in the usual way after the ferric hydroxide has been collected. Soluble barium salts are detected by the addition of sulphuric acid. For the detection of cyanides, the water is acidified with sulphuric acid, a length of copper wire is introduced, and the solution distilled; the distillate is tested for hydrocyanic acid in the usual manner (formation of Prussian-blue). Mercury, if present, is deposited on the copper wire; should the latter exhibit a white colour, it is washed with alcohol, dried, and heated in a tube. The mercury will sublime, and may be identified by converting it into mercuric iodide. Lead and zinc may be separated from the water as sulphides, the water used for the previous experiments being used for the purpose. W. P. S.

Estimation of Benzene in Gas Mixtures. G. A. Burrell and I. W. Robertson (*J. Ind. Eng. Chem.*, 1915, **7**, 669–670).—The apparatus used consists of two glass bulbs, the upper bulb having a stem provided with a three-way tap; a side-tube on the stem carries a mercury manometer, and the upper bulb is filled with phosphoric oxide to remove moisture from the gas. After the air has been exhausted from the apparatus, the gas under examination is admitted at atmospheric pressure, the barometer read, and the two bulbs then immersed in a mixture of solid carbon dioxide and acetone or alcohol (this mixture gives a temperature of $-78°$). At the end of ten minutes, as much gas as is possible is removed from the apparatus by means of a pump. In the case of a mixture of coal-gas and water-gas, practically all the gases other than benzene are thus removed. The tap of the apparatus is now closed, the cooling mixture removed, the benzene vaporised at ordinary temperature, and its pressure read on the manometer. The pressure compared with the atmospheric pressure gives the percentage quantity of benzene in the gas mixture. W. P. S.

Estimation of Toluene in Commercial Toluols. D. Northall-Laurie (*Analyst*, 1915, **40**, 384—389).—Two hundred c.c. of the

sample are distilled from a flask of just sufficient capacity, with the neck cut off close above the side-tube. The liquid is distilled at the uniform rate of 7 c.c. per minute into a 50 c.c. cylinder; when 50 c.c. have been collected, the cylinder is changed quickly for a 100 c.c. cylinder, and when 98·5 c.c. have been collected, the burner is removed and the contents of the flask allowed to cool. By the time all drops from the condenser have ceased, 100 c.c. of the distillate will have been collected. Should the first 50 c.c. be turbid from the presence of water, it is shaken with a pellet of calcium chloride. The contents of the flask are now cooled under the tap, and transferred to a boiling-point apparatus. This consists of a flask with a short side-tube connected with a vertical tube, the lower end of which enters the side of the flask, whilst the upper end is attached to a reflux apparatus. In the neck of the flask is sealed a thin glass cylinder with a hole in the side corresponding with the opening to the side-tube; this glass screen protects the bulb of the thermometer from draughts. Reference should be made to the original for the exact shape and dimensions of this piece of apparatus, since the whole method depends on the way in which the boiling point is determined. The liquid is boiled at such a rate that the condensed liquid falls from the condenser at the rate of one drop per second. The observed boiling point is corrected for atmospheric pressure and length of the exposed mercury thread. The boiling point of the first 50 c.c. of distillate is then determined in the same way. On reference to a table or graph constructed from results obtained with known mixtures of benzene, toluene, and xylene, the quantity of toluene is read off A graph is given in the original, on which the percentage quantities of toluene and benzene present can be read off directly; the difference between the sum of these percentages and 100 represents the quantity of xylene. The method is trustworthy within 0·1%, and is applicable to all possible combinations of toluene with benzene and xylene when the samples contain from 50 to 100% of toluene. In the case of samples containing less than 50% of toluene, a known quantity of pure toluene should be added, so as to bring the results on the graph given. Any paraffin in the sample would appear in the analysis as toluene, but a correction may be made for its quantity by taking the specific gravity of the fractions b. p. 107° to 115°; every unit in the third place in the specific gravity less than the specific gravity of toluene (0·870) will represent 0·68% of paraffin in the quantity of toluene found. Carbon disulphide may be present in certain samples, but may be removed previously by treatment with alcoholic potassium hydroxide solution. W. P. S.

Hydrochloric Acid-Ethyl Ether Mixture as a Reagent for Rubber Analysis. Douglas F. Twiss (*India-Rubber Journal*, 1915, **50**, 199).—The ease with which a mixture of hydrochloric acid and ether penetrates rubber (compare Stevens, this vol., ii, 480) renders it useful for the destruction of accelerators of vulcanisation

in a compounded rubber before the extraction of free sulphur by hot acetone. D. F. T.

Practical Alcoholometry. H. P. BARENDRECHT (*Chem. Weekblad*, 1915, **12**, 736—741).—A comparison of the results obtained in determining the percentage of alcohol in aqueous solution by means of the pyknometer and alcoholometer. A. J. W.

The Estimation of Ethyl Alcohol in Ethyl Ether. P. SZEBERÉNYI (*Zeitsch. anal. Chem.*, 1915, **54**, 409—411).—The process is intended for samples in which the amount of alcohol is too small to be determined by means of the density, and is based on the fact that alcohol is readily oxidised by a moderately acid solution of potassium dichromate, whilst ether is but slightly affected.

Five c.c. of the sample are diluted with water up to 100 c.c. Thirty c.c. of this are placed in a 500 c.c. flask, into which has already been introduced 10 c.c. of $N/2$-dichromate, 20 c.c. of dilute sulphuric acid (1:1), and 40 c.c. of water. After boiling for fifteen minutes under a vertical condenser, and cooling, the excess of dichromate is titrated iodometrically. Anything above 0·9 c.c. of dichromate used represents 0·64 mg. of alcohol for each c.c. The exact quantity of dichromate used up by ether must be determined by experiment.

For somewhat larger amounts of alcohol, 5 c.c. of the aqueous solution are taken with 20 c.c. of the dichromate, 55 c.c. of water, and 20 c.c. of the dilute sulphuric acid. In such cases, no correction need be made for the dichromate used up by the ether.

If the ether is also to be estimated, a 2% aqueous solution is prepared, and 10 c.c. are treated for alcohol, as described. Another 10 c.c. are then placed in a stoppered 500 c.c. flask with addition of 40 c.c. of $N/2$-dichromate and 40 c.c. of sulphuric acid previously mixed with 10 c.c. of water, and cooled. After waiting for twelve hours, the contents of the flask are diluted with 400—500 c.c. of water, and the excess of dichromate is titrated as before.

After deducting the dichromate used up by the alcohol (multiplied by 1·1), from the result, the ether is found by multiplying the number of c.c. reduced by 4·6. L. DE K

Detection of β-Naphthol in Lysol and Similar Preparations. R. BODMER (*Analyst*, 1915, **40**, 341—342).—When 1 c.c. of lysol free from β-naphthol is dissolved in 100 c.c. of water, and the solution treated with 1 c.c. of diazotised benzidine reagent (prepared by diluting a mixture of 1 gram of benzidine, 4 c.c. of concentrated hydrochloric acid, and 1 gram of sodium nitrate to 100 c.c. with water, and neutralising the solution), an orange-coloured solution is obtained, but if as little as 0·2% of β-naphthol is present in the lysol, a red coloration is produced. The quantity of β-naphthol may be ascertained by comparing the coloration with that given under similar conditions by lysol containing a known amount of β-naphthol. Within certain limits, the differences in colour ex-

hibited by different quantities of lysol are distinct, and it is possible to distinguish between samples of lysol containing 0·2, 0·5, and 1% of β-naphthol respectively. W. P. S.

Staněk's Method for the Estimation of Sucrose. H. PELLET (*Bull. Assoc. Chim. Sucr. Dist.*, 1915, **32**, 169—173).—This method (A., 1914, ii, 586), when applied to molasses, yields results which agree with those given by Pellet's sulphurous method, Andrlík's carbamide method (compare A., 1914, ii, 750), Ogilvie's invertase method, and Saillard's method (A., 1914, ii, 682); of all these, the sulphurous acid method is considered to be the most simple and rapid. W. P. S.

Estimation of Reducing Sugars in the Presence of Sucrose. H. PELLET (*Ann. Chim. anal.*, 1915, **20**, 169—175).—Sucrose has a distinct reducing action when boiled for some time with Fehling's solution, the extent of the reduction varying with the duration of the boiling, the alkalinity of the Fehling's solution, the concentration of the sucrose, etc. Reduction does not, however, take place if the mixture of sucrose solution and Fehling's or cupropotassic solution (compare A., 1914, ii, 750) is heated to 62°, and maintained at this temperature for ten minutes. A small quantity of reducing sugar (0·01%) in the sucrose causes a reduction of the Fehling's solution under these conditions. W. P. S.

An Apparatus for the Photolysis of Powders. GUILBAUD (*Compt. rend.*, 1915, **161**, 212—213).—A description of a simple apparatus for carrying out photolytic tests of such substances as nitrocellulose and smokeless powders. It consists essentially of a quartz decomposition tube, 15 mm. wide and 100 mm. long, which is ground into a glass cap, through which connection is made by a short capillary tube to a sensitive volumeter by means of a three-way tap. A known weight of the substance is put into the decomposition tube, which is then connected to the apparatus and evacuated. Connexion is then made with the volumeter, the tube is submitted to the rays from a mercury vapour lamp for a given time, and the volume of gas evolved is measured from time to time. Finally, the gases are driven out of the volumeter through the three-way tap into a gas analysis apparatus. W. G.

Estimation of Formic Acid in the Presence of Acetic Acid. R. LAUFFMANN (*Chem. Zeit.*, 1915, **39**, 575).—A method proposed recently by Heermann for the estimation of formic and acetic acids in admixture depends on the decomposition of acetates by formic acid. The solution containing the two acids is neutralised with sodium hydroxide, evaporated to dryness, the residue dried at 125°, and weighed; it is then treated with formic acid, evaporated, again dried, and weighed. The amount of acetic acid present is calculated from the difference in the two weights obtained, and the formic acid is found by difference. The author finds that the decomposition of the acetate is never quite complete, even after

repeated evaporations with formic acid and water, and that the results obtained are, consequently, only approximately correct. In the case of solutions containing about 1% of the two acids together, and from 0·3 to 0·7% of formic acid, the quantity of formic acid found is about 0·02% too high, and the amount of acetic acid correspondingly low. W. P. S.

Detection of Hydrocyanic Acid in Toxicology by the Ferric Thiocyanate Test. P. LAVIALLE and L. VARENNE (*J. Pharm. Chim.*, 1915, [vii], **12**, 74—81).—The solution suspected to contain hydrocyanic acid is treated with ammonium sulphide, boiled for five minutes, and then evaporated to a volume of 1 c.c. This residual solution is mixed with 9 c.c. of water, ten drops of hydrochloric acid are added, and the solution is extracted several times with ether. The ethereal extracts are allowed to evaporate at the ordinary temperature, and the residue is treated with dilute ferric chloride solution, added drop by drop until any coloration obtained reaches its maximum intensity; an excess of ferric chloride is to be avoided. A red coloration indicates the presence of hydrocyanic acid. If the coloration is very slight, the mixture is shaken with 2 c.c. of ether; after separation, the ethereal layer will exhibit a violet coloration if only a very small quantity of hydrocyanic acid is present. Meconic acid yields a coloration with ferric chloride similar to that given by thiocyanic acid, but ferric meconate is insoluble in ether. The test will detect the presence of as little as 0·00005 gram of hydrocyanic acid. W. P. S.

Detection of Benzoic Acid and Salicylic Acid in Milk. PHILIPPE (*J. Pharm. Chim.*, 1915, [vii], **12**, 168—169; from *Pharmazevtizeski J.*, 1915, No. 8).—One hundred c.c. of the milk are treated with 40 c.c. of Fehling's copper sulphate solution, 10 c.c. of sodium hydroxide solution, and 150 c.c. of water, and the mixture is filtered. The filtrate is acidified with 5 c.c. of concentrated hydrochloric acid, extracted with ether, and the ethereal extract evaporated in a basin. The latter is then covered, heated, and any sublimate collecting on the cover is removed and examined microscopically and chemically. The test will detect the presence of 1 part of benzoic acid in 50,000 parts of milk. W. P. S.

Estimation of Fat in Food for Infants. H. G. CHAPMAN (*J. Roy. Soc. New South Wales*, 1914, **48**, 469—472).—The author records an instance where the ether extraction method for the estimation of fat in an infant's food gave 7·4%, as against 16·85% obtained by the Röse-Gottlieb method. The fats extracted in each case were identical. The cause of this discrepancy is not yet determined, but fairly correct figures were obtained by the ether extraction method when less than 0·75 gram of food were mixed previously with 10 c.c. of water, transferred to a filter-paper, the water driven off at 90°, and the dried filter-paper extracted with dry ether in a Soxhlet apparatus as usual. G. F. M.

Apparent Effect of Acetic Acid on the Constants of Butter Fat. CLARENCE BAHLMAN (*J. Ind. Eng. Chem.*, 1915, **7**, 680—681).—A convenient method of estimating fat in such substances as ice-cream consists in treating 9 grams of the sample with 20 c.c. of glacial acetic acid in an ordinary Babcock milk bottle, adding 10 c.c. of sulphuric acid, and proceeding as in the estimation of fat in milk; the acetic acid is added to prevent the charring action of the sulphuric acid on the sugar present. The volume of the fat layer multiplied by 2 gives the percentage quantity of fat in the sample. The authors attempted to identify the fat as butter-fat by separating the fatty layer and applying the usual tests, but the results obtained were untrustworthy. Even with products prepared from milk, the fat gave higher saponification and Reichert-Meissl numbers than were obtained with butter-fat, and the refractometer number was low. This was due to the retention of acetic acid by the fat, but it was found that it could be expelled by heating the fat at 95° for one hour. The heated fat then gave normal analytical results. Fats separated from dairy products by decomposition with sulphuric or hydrochloric acid did not retain any of the mineral acid. W. P. S.

Estimation of Phenacetin and Salol in Admixture. W. O. EMERY, G. C. SPENCER, and C. C. LEFEBVRE (*J. Ind. Eng. Chem.*, 1915, **7**, 681—684).—Two methods are described; in the first, the phenacetin is converted into phenetidine sulphate, the salol separated by means of chloroform, the phenetidine sulphate then reconverted into phenacetin, and weighed. Since a portion of the salol is lost by volatilisation, the quantity of this substance present is found by difference. The second method consists in converting the salol into sodium salicylate and phenoxide, separating and recovering the phenacetin by extraction with chloroform, and estimating the salol by titration with bromine. If the phenacetin and salol are present in pill or tablet form and mixed with other substances, the sample is extracted with chloroform, and the residue obtained on evaporating the chloroform solution used for the analysis. *First method.*—A weighed quantity of the two substances is heated on a water-bath with 10 c.c. of dilute sulphuric acid (1 : 10) until the volume of the solution has been reduced to 5 c.c.; 10 c.c. of water are added, the solution again evaporated to 5 c.c., and the addition of water followed by evaporation is repeated. The residual solution is extracted with three successive quantities of chloroform, the chloroform extracts are washed, as they are separated, with 5 c.c. of water, and the latter is added to the aqueous acid solution. The latter is treated with an excess of sodium hydrogen carbonate, 25 c.c. of chloroform are added, followed by five drops of acetic anhydride for every 0·1 gram of phenacetin known or believed to be present. After the mixture has been shaken thoroughly, the chloroform layer is separated, distilled, and the distilled chloroform used to extract the solution a second time; a third extraction is made in a similar manner, an additional quantity of chloro-

form being used to augment the volume of that distilled. The chloroform extract is washed with water, filtered, evaporated, the residue of phenacetin treated several times with water and evaporated, then dried over calcium oxide, and weighed. *Second method.*—A quantity of the two substances, containing not more than 0·1 gram of salol, is heated on a water-bath for five minutes with 10 c.c. of 2·5% sodium hydroxide solution, then cooled rapidly, and extracted with chloroform; the chloroform solution is washed with 5 c.c. of water, filtered, evaporated, and the residue of phenacetin dried and weighed. The aqueous alkaline solution and the water used for washing the chloroform extract are transferred to a stoppered bottle, diluted with water to 200 c.c., and an excess (about 45 c.c.) of *N*/7-potassium bromide-bromate solution is added, followed by 10 c.c. of concentrated hydrochloric acid. The mixture is shaken for one minute, and at intervals for thirty minutes; 10 c.c. of 15% potassium iodide solution are then added, the mixture is shaken for fifteen minutes, and the liberated iodine titrated with *N*/7-thiosulphate solution. Each molecule of salol requires 12 atoms of bromine, and 1 c.c. of *N*/7-bromide-bromate solution is equivalent to 0·002548 gram of salol. Both methods yield trustworthy results. W. P. S.

Identifying Amino-*H*-acids. BERNHARD C. HESSE (*J. Ind. Eng. Chem.*, 1915, **7**, 674—675).—The following tests are proposed for the identification of 2-amino-*H*-acid, 7-amino-*H*-acid, and 2:7-diamino-*H*-acid (*H*-acid is 1:8-aminonaphthol-3:6-disulphonic acid): (1) A small quantity (less than 1 mg.) of the substance is treated with a few drops of 40% sodium hydroxide solution, and then diluted with 1 c.c. of water. (2) A small quantity of the substance is heated with two drops of sulphuric acid (D 1·84) until a violet colour begins to develop; two drops of 0·5% sodium nitrite solution are then added, the mixture is cooled, diluted with 0·5 c.c. of water, nearly neutralised with 40% sodium hydroxide solution, and rendered alkaline with a slight excess of sodium carbonate. (3*a*) A trace of the substance is heated with one drop of saturated sodium carbonate solution, one drop of concentrated hydrochloric acid, and 0·5 c.c. of water are added, the mixture boiled and cooled, one drop of the solution is placed on a filter-paper, and one drop of hydrogen peroxide is added. (3*b*) When the coloration which develops on the paper has reached its maximum, the spot is treated with a drop of 40% sodium hydroxide solution. The colorations obtained in these tests are:

Test.	2-Acid.	7-Acid.	2 : 7-Acid.
1.	Yellow or brown.	Green.	Violet, then blue.
2.	Bluish-red.	Bluish-red.	Yellow or brown.
3*a*.	Brown or yellow.	Violet to red.	Blue.
3*b*.	Red.	White or cream.	Red to violet.

W. P. S.

Estimation of Small Quantities of Alkaloids. E. CARLINFANTI (*Boll. chim. farm.*, 1915, **54**, 321—323).—The estimation of small

amounts of morphine or codeine, either in pharmaceutical preparations or for toxicological purposes, may be effected by the following colorimetric methods, a Wolff colorimeter being employed.

In the case of morphine, the solution to be examined and a known volume, say 1 c.c., of a 0·5% morphine hydrochloride solution are evaporated separately in basins on a water-bath, and allowed to cool in a desiccator. Each of the residues is dissolved in 5 c.c. of concentrated sulphuric acid, and the liquid introduced into a tube holding about 50 c.c. and fitted with a ground stopper; each dish is washed thrice with 3 c.c. of concentrated sulphuric acid, and the washings added to the tube, which is then closed and immersed for fifteen minutes in a boiling water-bath. To the cooled tubes are added 10 c.c. of a mixture of 100 c.c. of concentrated sulphuric acid with two drops of nitric acid (D 1·4); on shaking the tubes, the characteristic, blood-red coloration appears. The solutions are then introduced into the cylinders of the colorimeter, in which they are made up to the same height by addition of the small quantities of concentrated sulphuric acid used for washing the tubes.

In the case of codeine, to each of the two aqueous residues, reduced to about 1 c.c. by evaporation on a water-bath at 70—75°, 15—20 c.c. of monohydrated sulphuric acid are added cautiously so that the mixture is not heated. The liquid is then introduced into a 50 c.c. flask, together with three quantities of 5 c.c. of the acid used to wash out the dish and 10 c.c. of monohydrated sulphuric acid containing 2 c.c. of 10% ferric chloride solution per 100 c.c. of the acid. After being shaken, the flasks are immersed for fifteen minutes in a water-bath at 80°, the cooled solutions, which have assumed blue colorations, being introduced into the cylinders of the colorimeter as before.

These methods admit of the estimation of 0·001—0·003 gram of morphine or codeine hydrochloride to within about 0·0001 gram.

T. H. P.

A New Very Sensitive Colour Reaction for Atropine, Hyoscyamine, and Scopolamine. R. WASICKY (*Zeitsch. anal. Chem.*, 1915, **54**, 393—395).—The reagent consists of a solution of 2 grams of *p*-dimethylaminobenzaldehyde in 8 grams of sulphuric acid, to which 0·4 gram of water is then added. The three above-mentioned alkaloids are not affected by the reagent in the cold, but on gentle warming an intense red colour appears which, after removing the source of heat, becomes more and more cherry-red and then reddish-violet, the colour persisting for days.

Several alkaloids also give similar colorations, but these take place at once in the cold; some give on warming a colour of quite a different shade. It is believed that the reaction is not due to tropine, but to tropic acid groups. L. DE K.

Goeldner's Test for Cocaine. LEON A. RYAN (*J. Amer. Chem. Soc.*, 1915, **37**, 1960—1961).—The above test (*Zeitsch. anal. Chem.*, 1901, **40**, 820) consists in adding the suspected solid to a mixture

of about 0·01 gram of resorcinol with six or seven drops of "pure" sulphuric acid, when a "cornflower-blue" colour should develop. It is now found that this is not a test for cocaine at all, but that the colour is caused by nitrates or nitrites. On evaporating 1 c.c. of a solution containing one ten-millionth of a gram of nitrogen as potassium nitrate, moistening the residue with pure sulphuric acid, and then adding a trace of resorcinol, the blue coloration is quite distinct. J. C. W.

Estimation of Creatine in Muscle and other Organs. N. W. JANNEY and N. R. BLATHERWICK (*J. Biol. Chem.*, 1915, **21**, 567—582).—Creatine and creatinine are probably not to be regarded as existing in firm combination in liver and muscle; acid hydrolysis of such organs, previously freed from these substances by extraction, fails to yield additional creatine or its anhydride. The methods of estimation described previously leave much to be desired. Folin's procedure cannot be recommended; other substances present may affect the colour reaction and lead to errors of more than 400% in liver and other organs; even in muscle there is usually some error. The method recommended consists in simple extraction with boiling water to which a little acetic acid is added; the addition of aluminium hydroxide assists in the coagulation of the proteins; the conversion of creatine into creatinine should be carried out in the water-bath; after this, Folin's procedure can be followed. W. D. H.

Titration of Opium. DOHME (*Ann. Chim. anal.*, 1915, **20**, 182—183; from *J. Amer. Pharm. Assoc.*, 1915, 85).—Four grams of the powdered opium are shaken with water for three hours, then washed thoroughly, the aqueous extract is evaporated to 50 c.c., rendered strongly alkaline with sodium hydroxide, and extracted several times with ether. The aqueous solution is now acidified with sulphuric acid, next rendered slightly ammoniacal, and the morphine extracted with a mixture of equal parts of chloroform and *iso*butyl alcohol. After the chloroform has been evaporated from the extract, the *iso*butyl alcohol is removed by distillation under reduced pressure; the residue is then dissolved in a known volume of standard acid, and the excess of the acid titrated, using methyl-orange as the indicator. W. P. S.

Group Method for the Detection of Gelatinising Agents, Pasty Material and Thickeners, Used in Food Products. LEON A. CONGDON (*J. Ind. Eng. Chem.*, 1915, **7**, 606—607).—The substances are divided into six groups, according to their reactions with various reagents. (1) With iodine solution: starch, blue coloration; amylodextrin, purple coloration; erythrodextrin, red coloration; achroodextrin, no coloration. (2) With acid mercuric nitrate solution; gelatin, turbidity; acacia, gelatinous precipitate soluble in excess of the reagent; agar or tragacanth, white, cloudy precipitates. (3) With concentrated sodium borate solution: agar or acacia, white precipitates (acacia also gives a white precipitate

with basic lead acetate and a bluish-black coloration with tannin). (4) With sodium hydroxide solution: tragacanth, brownish-yellow coloration on heating; acacia, white precipitate. (5) With mercuric chloride solution: dextrin, turbidity; albumin and gelatin, white precipitates. (6) With ammoniacal copper solution: pectin, microscopic crystals of cupric pectate. W. P. S.

Culture Media Employed for the Bacteriological Examination of Water. I. The Schardinger-Dunham Medium for Detecting Bacteria which Produce Hydrogen Sulphide. E. M. CHAMOT and H. W. REDFIELD (*J. Amer. Chem. Soc.*, 1915, **37**, 1606—1630).—Slight variations in concentration of the media used in the bacteriological examination of water may lead to considerable differences in the results, and a study has therefore been made of the various culture media employed with the object of finding a really satisfactory standard medium. An account is now given of experiments with the Schardinger-Dunham medium (A., 1898, ii, 193), to which artificial sewage was added. Observations were made of the influence on the growth of the bacteria of the concentrations of the peptone and the inorganic salt (sodium chloride), and of the acidity of the medium.

It was observed that the rapid production of large quantities of hydrogen sulphide by sewage organisms is due to a group of bacteria which do not actively ferment carbohydrates, rather than to members of the colon bacillus group. E. G.

Culture Media Employed for the Bacteriological Examination of Water. II. Lactose-Peptone Media. E. M. CHAMOT and C. M. SHERWOOD (*J. Amer. Chem. Soc.*, 1915, **37**, 1949—1959. Compare preceding abstract).—A study has been made of the effect of the concentration of the nitrogenous matter, inorganic salts, acids, and carbohydrates of lactose-peptone media on the volume and composition of the gases evolved during the development of the fermentative bacteria of the *B. coli* group. It is found that: (1) the volume of the gas increases to a maximum with the concentration of the nitrogenous food; (2) the addition of from 0·5 to 1% of potassium chloride stimulates fermentation, whilst sodium chloride and other salts do not give such uniformly good results; (3) it is unprofitable to use a more than 1% solution of lactose; and (4) fermentation is most rapid when the mixture has an acidity of about 1%, expressed in c.c. of *N*-hydrochloric acid, with phenolphthalein as indicator. The question of the composition of the gases evolved is reserved for another paper.

A very sensitive and stable peptone medium consists of peptone 3—4%, lactose 0·8%, potassium chloride 0·6%; the reaction should be equivalent to +1% of *N*-HCl. J. C. W.

General and Physical Chemistry.

The Reflection Capacity of Certain Solutions in the Ultra-red Spectrum. F. GEHRTS (*Ann. Physik.*, 1915, [iv], **47**, 1059—1088).—The reflection capacity of water and aqueous solutions of salts has been examined in the region 1·0—11·5 μ. In general, small differences are found when the wave-lengths of the reflection maxima for the solid salts are compared with those for the same substances in solution.

From experiments with solutions of ammonium nitrate and ammonium sulphate of widely varying concentration, it appears that the reflection capacity increases more rapidly than the concentration. The position of the maximum is displaced in the direction of the visible spectrum when the concentration is increased. Both effects are shown to be in agreement with Drude's theory of dispersion. H. M. D.

The Ultra-violet Spectrum of Elementary Silicon. J. C. MCLENNAN and EVAN EDWARDS (*Phil. Mag.*, 1915, [vi], **30**, 482—484).—The spectrum of silicon described by Crookes (A., 1914, ii, 693) has been supplemented by measurements of the wave-lengths of lines in the spark spectrum between λ 2124·4 and λ 1842·2. The silicon used was from the same source as that used by Crookes. H. M. D.

A New Series of Lines in the Spectrum of Univalent Helium. JOHN KOCH (*Ann. Physik.*, 1915, [iv], **48**, 98—108).—The spectrum which is emitted by helium canal rays when subjected to the action of a strong electric field has been found to contain lines which do not belong to any of the recognised helium series. The wave-lengths of the two new lines are λ 4518·77 and λ 4046·02. They are strongly polarised, the polarisation of the component which vibrates parallel to the field being much stronger than that of the component at right angles. It is shown that the two lines belong to a combination series, which, according to the Ritz formulation, is given by the equation $\nu = (2, p, \pi) - (m, p, \pi)$, where $m = 3, 4, 5, \ldots$ and p and π are the series constants of the principal series. The lines are due to helium atoms carrying a single charge, and it is to be noted that the series is analogous to series which have already been observed for lithium and sodium. It is to be expected that the doubly charged helium atoms will give rise to a similarly constituted series of lines. H. M. D.

Spectroscopic Examination of Two Sardinian Minerals. E. SERNAGIOTTO (*Gazzetta*, 1915, **45**, ii, 86—96).—Results are given of a spectroscopic study of plates of black mica and of a red pigment, both obtained from the granulites of Cala Francese, Isola di Maddalena (compare Lovisato, A., 1913, ii, 613). T. H. P.

Extinction Measurements of Solutions of Sulphurous Acid, Sulphites, Hydrogen Sulphites, and Metabisulphites, and of Gaseous and Liquid Sulphur Dioxide. CHARLES SCOTT GARRETT (T., 1915, **107**, 1324—1334).—Extinction measurements have been made with 0·06 $SO_2/2$ solutions of sulphurous acid, rubidium hydrogen sulphite, potassium hydrogen sulphite, sodium hydrogen sulphite, ammonium sulphite, sodium metabisulphite, potassium metabisulphite, acetone sodium hydrogen sulphite, potassium sodium sulphite, sodium sulphite, and symmetrical and unsymmetrical diethyl sulphites. These measurements were carried out with a large Hilger quartz spectrometer, using a rotating sector and a nickel spark as illumination. The extinction curve for the acid was easily obtained, and was easily reproducible; in the case of the acid sulphites, it was shown that the absorption increased with time, and that a maximum absorption was obtained in four or five weeks. This behaviour, on being further studied, was shown to be due to the influence of light, for freshly prepared solutions exhibited no selective absorption, and when kept in the dark still exhibited no selective absorption, but solutions exposed to light for twenty-six days exhibited the maximum absorption. Metabisulphites behaved in exactly the same way as the acid sulphites. The normal sulphites of sodium and potassium, mixed sulphites of sodium and potassium and of silver and potassium, the two diethyl sulphites and acetone sodium hydrogen sulphite, were all without selective absorption. Consequently, it follows that the present method of investigation is incapable of furnishing evidence as to the constitution of sulphites. The seat of the selective absorption is shown to be hydrated sulphur dioxide, SO_2,xH_2O, and the changes in the absorption are to be explained by the equations: (1) $Na_2S_2O_5+H_2O=2NaHSO_3$; (2) $NaHSO_3+NaHSO_3 \rightleftarrows Na_2SO_3+H_2SO_3$ (light reaction); (3) $H_2SO_3 \rightleftarrows SO_2,xH_2O$; and (4) $R{\cdot}R'SO_3+H_2O=RHSO_3+R'{\cdot}OH$. The relative quantity of SO_2,xH_2O present in equally concentrated solutions of the various acid sulphites is calculated, and these quantities are shown to increase with increasing strength of the base, that is, the equilibrium given by equation (2) shifts to the right the stronger the base.

The adsorption of gaseous, liquid, and solution of sulphur dioxide of concentration 0·06 $SO_2/2$ were then compared, and the centre of absorption in the three cases found to be 2961 Å.U. for the gas, 2850 Å.U. for the liquid, and 2770 Å.U. for the solution.

J. F. S.

Light Absorption and Fluorescence. III. E. C. C. BALY (*Phil. Mag.*, 1915, [vi], **30**, 510—526. Compare A., 1914, ii, 318; this vol., ii, 77).—According to Bjerrum (A., 1912, ii, 1114), the frequencies of lines in the short-wave infra-red absorption spectrum can be represented by the formula $\nu \pm hn/2\pi^2 I$, in which ν is the frequency of the central line of the group, I the moment of inertia of the rotating molecules, h the Planck constant, and n the series of whole numbers 1, 2, 3, etc. The further application of

Bjerrum's views has shown that the above formula is applicable to the whole of the absorption-band groups in the short-wave infra-red, the visible and the ultra-violet regions of the spectrum.

The essence of Bjerrum's theory is that the frequencies of the centres of the infra-red bands are consecutive multiples of a fundamental constant or basis, and in so far it agrees with experiment, but the theory offers no explanation of the fact that certain multiples of the constants correspond with absorption bands which are of much greater intensity than the neighbouring multiples on each side. To account for these differences of intensity, it is suggested that there are two (or more) constants or bases, and that the intensity of an infra-red is especially marked when its frequency is either an even multiple of the two constants or represents the least common multiple of these numbers.

By application of the Bjerrum principle of combination, and the use of four fundamental constants, it is shown that the wave-lengths of the whole of the absorption lines in the ultra-violet absorption spectrum of benzene can be calculated, and that the results are in good agreement with the measured wave-lengths.

From an examination of the infra-red spectra of phenol, aniline, myricyl alcohol, and triethylamine, it has been found that the spectra are additively related to the spectra of the constituent radicles. The wave-lengths of the ultra-violet absorption lines of phenol and aniline may thus be calculated by making use of the constants which are characteristic of the infra-red spectra of benzene and water and of benzene and ammonia, respectively. The agreement is quite satisfactory, and well within the limits of experimental error. H. M. D.

Absorption Spectra of Certain Aromatic Nitroamines and Nitroamides. II. GILBERT T. MORGAN, HENRY WEBSTER MOSS, and JAMES WALKER PORTER (T., 1915, **107**, 1296—1318; compare T., 1911, **99**, 1945; 1912, **101**, 1210).—The absorption spectra of $M/5000$-alcoholic solutions of a large number of nitroamines and nitroamides have been measured by means of a single-prism Hilger spectrometer, using a molybdenum spark as source of illumination. These included nitroanilines, aminotoluenes, nitroaminoxylenes, and their alkyl, aryl, and other derivatives, nitropiperidines, nitro-*p*-phenylenediamine and its acetyl derivatives, 4-nitro-2:5-tolylenediamine, nitroaminophenols, *o*-dinitrotolidine (I and II), and *m*-dinitrotolidine (I, II, III, and IV). In all cases, absorption curves, melting points, and colour of the substances investigated are given. The general results of the present paper and the two previous papers (*loc. cit.*) are summarised in the paper. It is shown that it is extremely difficult to express the influence of substitution and intramolecular change on the visible and ultra-violet spectrum. The rule (Hartley, T., 1881, **39**, 165; 1885, **47**, 693; 1903, **83**, 224) that the substitution of a methyl group for hydrogen effects a shift of the absorption towards the red is not generally fulfilled among aromatic derivatives. In some cases the conversion of amino-compounds into fully hydrogenised piperidine

rings causes the absorption band to become more persistent and to be shifted toward the red. In the case of 3:5-dinitro-4-piperidino-*o*-xylene, however, the band entirely disappears. The introduction of a second nitro-group into nitro-compounds causes a shift of the single broad band toward the blue, but the introduction of a third nitro-group leads to the appearance of two bands, the second of which is lost by alkylation, arylation, or benzylation. The acylation of nitroamines either obliterates the absorption band completely or greatly reduces its persistence, and shifts it towards the blue. With regard to the relationship between chemical constitution of aromatic compounds and their absorption spectra, it is shown that the experimental results indicate that the differences manifested in the selective absorption of closely related organic substances are due to specific differences in chemical structure which are too subtle to be represented by the present conventional modes of representing constitution. It follows, therefore, that each organic substance of any considerable degree of complexity must be regarded as having its own particular constitution in regard to its action on visible and invisible light. The resultant absorption is a specific characteristic of the compound, which, in general, cannot be deduced as an additive property obtainable by integrating the individual contributory effects of each of the constituent groups or atoms in the molecule. J. F. S.

Spectrographic Study of Amino-acids and Polypeptides. PHILIP ADOLPH KOBER [With WALTHER EBERLEIN] (*J. Biol. Chem.*, 1915, **22**, 433—441).—The absorption of aliphatic amino-acids in acid or alkaline solution is only general in the extreme ultra-violet. The aromatic amino-acids show absorption bands which may be useful in detecting them in peptide chains; excess of alkali increases the absorption and tends to shift it towards the red. The spectrum of di- and tri-peptides shows no special absorption. The keto-enol tautomerism in peptide linkings (Dakin and Dudley) is doubtful. W. D. H.

Quantitative Light-filter for the Ultra-violet Portion of the Spectrum. N. P. PESKOV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 918—942).—By the qualitative investigation of spectrograms, the author has devised a light-filter, in which gaseous bromine and chlorine are used in conjunction, which absorbs the spectral region 500—300 $\mu\mu$. By means of an improved modification of Henri's photographic method (A., 1911, ii, 833; 1912, ii, 873, 883, 964, 1132) for determining coefficients of absorption in the invisible part of the spectrum, these coefficients have been measured for gaseous chlorine and bromine for forty-three lines of the spectrum of the quartz lamp. The process of absorption of light in mixtures of several absorbing components is formulated mathematically, and by means of the formulæ deduced it is shown experimentally that, when dry chlorine and bromine are mixed, the characters of their absorption remains unchanged, Beer's law being consequently obeyed.

The light-filter has been subjected to detailed quantitative in-

vestigation, concentrations of bromine and chlorine being found which permit of the filtering of any part of the spectrum chosen beforehand; this filtration may be restricted within such narrow limits as 250 and 240 $\mu\mu$. T. H. P.

The Fluorescence of Sulphur, Selenium, and Tellurium Vapours. D. DIESTELMEIER (*Zeitsch. wiss. Photochem.*, 1915, **15**, 18—55. Compare Steubing, A., 1913, ii, 816).—Sulphur, selenium, and tellurium are found to give a fluorescent emission when the vapours of the elements are subjected to the influence of either white light or the light emitted by the arc burning between electrodes of various metals. In the case of sulphur vapour, the phenomenon is also observed when spark discharges are used as the source of excitation. The fluorescence is only observable when the vapours are of low density compared with that of the saturated vapours, and the influence of temperature on the intensity of the effect would seem to show that centres of emission are the diatomic molecules. The phenomenon is very sensitive to foreign substances, and no fluorescence is observed in the presence of small quantities of impurities.

The fluorescence spectra consist of bands which are shaded off towards the red end of the spectrum. As the atomic weight increases, the "centre of gravity" of the exciting light shifts from the ultra-violet into the visible region. In each case, changes are found to occur in the fluorescence spectrum when the nature of the exciting light is changed.

The absorption spectra of the free vapours have also been examined. These also consist of bands which are shaded off towards the red. With increasing atomic weight, these bands show an increasing tendency towards resolution into lines. In the case of selenium and tellurium, the absorption and emission spectra overlap to an appreciable extent, and the wave-length measurements afford evidence in support of the view that some of the fluorescent bands are coincident with bands in the absorption spectra. H. M. D.

Influence of Constitution on the Rotatory Power of Optically Active Substances. VIII. H. RUPE (*Annalen*, 1915, **409**, 327—357).—By the reaction between chloromethylenecamphor and a Grignard reagent, derivatives of methylenecamphor,

$$C_8H_{14}\begin{cases}C{:}CHR\\ CO\end{cases},$$

in an optically pure state are easily prepared. Substances in which R is methyl, ethyl, propyl, *iso*butyl, phenyl, benzyl, phenylethyl, phenylpropyl, *cyclo*hexyl, or α-naphthyl have been obtained; their description will be given in a future paper. Their optical investigation confirms the generalisations regarding the influence of certain groups on the rotatory power already recorded (A., 1909, i, 927; 1910, i, 398; 1913, i, 264, 266, 884; 1914, i, 131).

The $[\alpha]$ values for the C, D, E, and F lines at 20° in a 10% solution in benzene (liquid compounds are examined without a solvent) of these substances are recorded. The coefficient of the

rotatory dispersive power, $[\alpha]_F/[\alpha]_C$, is 2·31. The use of these data in calculating the dispersion curves of optically active homologous compounds has been recorded by Hagenbach (this vol., ii, 302). The author has observed that for most of the derivatives of methylenecamphor $[\alpha]_F - [\alpha]_C$ is almost exactly equal to $[\alpha]_D$. A similar result has been observed in the dispersion curves of some hydrocarbons derived from citronellaldehyde, where

$$[\alpha]_F - [\alpha]_C = [\alpha]_C$$

(Rupe and Jagers, A., 1914, i, 131). Consequently, for substances belonging to the same class of compounds, $[\alpha]_F - [\alpha]_C$ is a constant (compare also Walden, A., 1903, i, 311; Guye and Wassmer, A., 1904, i, 471). The same observation has also been noted in the case of a number of esters of menthol and myrtenol. The constant is best expressed as a function of a wave-length, λ_α, called the "characteristic wave-length," calculated by a formula,

$$1/\lambda_\alpha^2 = (1/\lambda_C^2 - 1/\lambda_D^2)([\alpha]_F - [\alpha]_C - [\alpha]_E)/([\alpha]_C - [\alpha]_D) + 1/\lambda_E^2,$$

deduced by Hagenbach (*loc. cit.*). The course of a dispersion curve is completely characterised by the characteristic wave-length, which is situated nearer the red end of the spectrum the flatter is the curve. The constant is an additive magnitude modified by constitutive influences.

The application of the characteristic wave-length in attacking the problem of anomalous rotatory dispersion is discussed. C. S.

Photochemical Reactions and the Photoelectric Effect. G. S. Landsberg (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 908—918).—The author advances the view that the influence of insolation on a reacting mixture produces a photoelectric effect, which results in ionisation, and thus activates the compounds, chemical changes gradually ensuing. In order to decide what directs this ionising action, the structures of atoms and molecules are briefly considered. Three kinds of electrons exist, bound by forces of varying strengths: (1) Constitutional or intra-atomic electrons, which enter into the composition of the atom itself, and are held so firmly to the central nucleus that, in most cases, an enormous amount of energy is necessary to detach them. (2) Interatomic or intramolecular electrons, which are not necessary to the existence of the atoms, but serve only to establish linkings between atoms, that is, to combine atoms to form molecules. (3) Intermolecular or free electrons, which pass freely from one molecule to another, and by their presence explain the phenomenon of metallic conduction.

It seems natural to assume that the photoelectric effect is accompanied by liberation of the electrons of valency, and experiment shows, indeed, that the sensitiveness to light of halogen salts of copper diminishes with increased stability of the compounds, whilst highly stable halogen salts, such as those of sodium and potassium, exhibit no effect. Photochemical reactions differ, therefore, from thermal chemical reactions, since their initial stages, that is, the activation of the molecules, proceed under the influence of an external cause, and are not conditioned by the thermal motion of the molecules, which is of internal origin. This distinction throws

light on the differences between the temperature-coefficients of reactions taking place in the dark and those of photochemical reactions. The former have values of 2—4 per 10°, whilst the latter form three groups, having the respective values $1{\cdot}04 \pm 0{\cdot}03$, $1{\cdot}20 \pm 0{\cdot}03$, and $1{\cdot}39 \pm 0{\cdot}03$, none of which differs greatly from 1. Since the photoelectric effect does not depend on the temperature, the same will be the case with the first stage of the photochemical reaction, namely, the ionisation of the molecules, and the influence of temperature is felt only later, when the increased velocity of the molecules increases the probability of collisions between them. With reactions in the dark, the effect of temperature is twofold, and the magnitudes of the temperature-coefficients are, on the average, greater than with photochemical reactions. T. H. P.

Laws of Photochemical Reactions with Interrupted Illumination. P. Lazarev (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 958—964). —In his communications on the theory of vision (*Pflüger's Archiv*, 1913, **154**, 459; 1914, **155**, 310; *J. Russ. Phys. Chem. Soc.*, Phys. Part, 1915), the author has shown that, with a sufficiently frequent interruption of a constant source of light, the actions on the light-sensitive pigments of the eye will be identical with those produced by a constant light source, provided that the amounts of energy introduced in the period of a change of brightness are the same in the two cases. This represents Talbot's law in photometry, which thus corresponds with a definite law in the photochemistry of the pigments of the eye, connecting the decomposition with the quantity of incident energy. It is now shown mathematically, and confirmed by a number of quoted examples, that this law is not confined to the special case of the photochemical reactions occurring in the eye, but is applicable to all photochemical reactions, of whatever complexity, and is, indeed, one of the fundamental laws of the chemical action of light. T. H. P.

Action of Ultra-violet Rays on Mercuric Chloride in Solution and on some Mercury Salts. Jean Pougnet (*Compt. rend.*, 1915, **161**, 348—351).—Mercuric chloride in aqueous solution is readily decomposed by ultra-violet rays, mercurous chloride being deposited. The action is rapid at first, but very soon slows down. The action is reversible, mercurous chloride in suspension in water being converted into mercuric chloride, slowly at first, but much more rapidly as the action proceeds. An examination of the action of ultra-violet rays on a large number of mercury salts in the dry or moist state showed that the action is rapid in nearly every case, the salts being most resistant when perfectly dry. W. G.

Variation of the Temperature-coefficients of Photochemical Reactions with the Wave-length. M. Padoa and Teresa Minganti (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 97—101. Compare Padoa and Zazzaroni, this vol., ii, 678).—The authors have measured the temperature-coefficients of Eder's reaction,

$$2HgCl_2 + (NH_4)_2C_2O_4 = 2HgCl + 2NH_4Cl + 2CO_2,$$

proceeding under the influence of lights of various wave-lengths. Besides white light, ultra-violet light with the luminous zone $\lambda=400$—280, and maximum intensity at $\lambda=366$, dark blue with the zone $\lambda=478$—410 and the maximum at $\lambda=448$, and green with the zone $\lambda=540$—505 and the maximum at $\lambda=533$, were used. In the case of the green light, the reaction proceeds so slowly that a little dilute aqueous tetrabromofluorescein was added as a sensitiser; the latter was also employed in some of the experiments with white light.

For the temperature interval 20—40°, the temperature-coefficients are as follows: white light, 1·29; ultra-violet, 1·05; dark blue, 1·21; green, with sensitiser, 1·75; white, with sensitiser, 1·50. In accordance with the results previously obtained with phototropic substances, the temperature-coefficients increase with the wave-length of the activating light. With white light, the sensitiser used raises the temperature-coefficient considerably, since it gives preponderance to the action of the yellow and green rays, which without it are of slight activity. Red light has no action, even in presence of a sensitiser.

Certain evidence indicates that, in the assimilatory process of plants under the influence of chlorophyll, the temperature-coefficient is considerably greater than 1.

In the light of the above results, the view usually accepted, that photochemical reactions are always characterised by temperature-coefficients approximating to 1 (compare Berthelot, this vol., ii, 329), requires modification. T. H. P.

Photoactivity of Blood. Walther Gerlach (*Zeitsch. Elektrochem.*, 1915, **21**, 425—426).—Wermel (*ibid.*, 1913, **19**, 811) has stated that blood, when it has been subjected to Röntgen rays, becomes photoactive. Schläpfer, on the other hand, states that it is capable of acting on a photographic plate whether it has been subjected to Röntgen rays or not (*Berl. klin. Woch.*, 1905, 1185). The author has repeated these experiments, and finds that both blood which has been subjected to Röntgen rays and fresh, untreated blood act on a photographic plate. The action, however, is not due to photoactivity on the part of the blood, but to vapours which rise from the blood. Similar effects are produced if water is substituted for blood. J. F. S.

Relation Between the Life of Radioactive Substances and the Range of the Rays Emitted. F. A. Lindemann (*Phil. Mag.*, 1915, [vi], **30**, 560—563).—A theory is put forward to account for the two quantitative laws of radioactivity, the exponential law of the rate of change and the Geiger-Nuttall relation between the radioactive constant λ and the range R of the α-particle expelled, $\log\lambda=A+B\log R$, where A and B are constants. Similar considerations may later be found to hold for β-ray changes. The first assumption is that the nucleus, supposed to consist of separate particles in movement, becomes unstable when N separate particles all pass some critical position within the short time τ, and the

second is that τ is the time for a strain to traverse the nucleus, just as a number of small impulses applied to a pendulum will lead to a maximum displacement if all are applied while the pendulum is moving in the same direction. The energy of the oscillating or rotating particles is $E=h\nu$, where ν is the frequency or number of times per second through which the particle passes the critical region. The probability of its being there in the interval τ is $\tau\nu$, and the probability of all N-particles being in the critical region is $(\tau\nu)^N$. This leads to the result that out of X atoms the number exploding in time dt is $dX=-X(\tau\nu)^N dt$, so that the radioactive constant λ is equal to $(\tau\nu)^N$, that is, to $(\tau/h)^N E^N$.

On inserting this value into the equation connecting λ and R, and calculating τ on the assumptions that the velocity of propagation is that of a sound wave in the nucleus, which is treated as continuous, and that the forces are electrical, it is deduced that for the Geiger-Nuttall relation to be true, N, the number of particles determining instability, must be the constant, $3/2\,B$, and the same for all three families, namely, 80, which, since the atomic numbers lie between 80 and 90, seems to show that nearly all the free positive particles in the nucleus must conspire together to bring about its disintegration. The radius of the nucleus can be evaluated from the magnitude of the constant A, and for radium works out to be $3{\cdot}85\times10^{-13}$, which is in fair agreement with that calculated for the gold nucleus by Sir E. Rutherford from the scattering of α-rays. F. S.

Excitation of γ-Rays by β-Rays. JADWIGA SZMIDT (*Phil. Mag.*, 1915, **30**, 220—224).—A source of radium-*D* in equilibrium with radium-*E* was placed in a strong magnetic field at some distance behind thin sheets of iron, nickel, copper, or zinc, and the ionisation due to the transmitted primary γ-rays measured in an electroscope filled with methyl iodide vapour. The sheets were then moved close to the source, and the secondary γ-rays produced by the β-rays caused a large increase in ionisation, that from the secondary γ-rays being regarded as the difference between the ionisations in the two dispositions. The absorption curve of this difference radiation in aluminium was exponential, and the absorption coefficients for the four metals were nearly the same as those found by Barkla and Sadler for the characteristic X-rays of these metals. For silver and tin, with a different experimental disposition, absorption coefficients agreeing with the "*L*" series of characteristic X-rays were obtained. These results and those of Richardson (A., 1914, ii, 697) leave no doubt of the identity of secondary rays excited by any stimulus, whether X-rays or β-rays from different sources, with the characteristic secondary X-rays of the elements. F. S.

Delta Radiation Emitted by Zinc when Bombarded by α-Rays. J. C. MCLENNAN and C. G. FOUND (*Phil. Mag.*, 1915, [vi], **30**, 491—502).—Previous experiments have shown that the δ-rays

emitted by a carbon plate under bombardment of α-rays increased considerably at liquid-air temperature, owing to occlusion of gas by the surface, and that gas occluded on the surface of metals is the cause of the photoelectric effect and the contact difference of potential. Potassium distilled repeatedly in a high vacuum shows no photoelectric effect, and zinc and bismuth similarly treated show little contact difference of potential with platinum until air is admitted. An arrangement was constructed which allowed of a zinc surface being coated in a high vacuum with vapour of zinc and then bombarded with α-rays, and its δ-radiation measured. Before this treatment, the zinc showed an emission of about three δ-ray electrons per α-particle striking it in a very high vacuum, but the number continually decreased with time, due to the removal of condensed gas from the surface. A freshly deposited zinc surface showed initially no emission of δ-ray electrons under the bombardment of α-rays, but in course of time the emission gradually developed, due to the gradual absorption of gas by the fresh surface. F. S.

The Action of Penetrating Radium Radiation on Inorganic and Biocoloids. A. Fernau and W. Pauli (*Biochem. Zeitsch.*, 1915, **70**, 426—441).—For this series of experiments, 78·6 mg. of radium in the form of radium barium carbonate were employed. Radiation was found, generally, to cause the precipitation of electropositive inorganic colloids, whereas it was without action on electronegative. This statement was illustrated by experiments with ferric hydroxide sol, cerium hydroxide, which readily formed a gel under the influence of the emanation, and vanadium pentoxide, which is unaffected, except to a small extent, owing to the formation of hydrogen peroxide. The changes were also traced by measurement of the viscosity changes during radiation. In the case of cerium hydroxide, there is a latent period of about twelve hours before viscosity changes can be detected. The action of radiation on coagulated (suspensoid) egg-albumin and native, well-dialysed albumin was also investigated. The coagulation of the former was examined in the presence of acetate mixtures of varying hydrion concentration. It was found that both on the acid and alkaline sides of the isoelectric point, radiation caused agglutination of the suspensoid. The action of rays on native albumin was to cause an irreversible change in the protein, resulting, finally, in coagulation. Radiation also causes increased coagulability by heat (diminution of coagulation temperature) and increased precipitability by alcohol. Unlike the coagulated protein, the agglutination of which by radiation is accelerated by salts, the native albumin is protected from coagulation by these substances. S. B. S.

Ionic Mobilities in Hydrogen and Nitrogen. W. B. Haines (*Phil. Mag.*, 1915, [vi], **30**, 503—509).—The experiments of Franck (A., 1909, ii, 953), who showed the presence of free electrons, characterised by high mobilities, in ionised nitrogen, helium, and

argon, which were extremely sensitive to the presence of impurities, have been repeated for nitrogen, and the effect of impurities examined quantitatively. Traces only of iodine, chlorine, sulphur dioxide, nitrous oxide, carbon disulphide, and chloroform destroy these negative ions of high mobility in nitrogen, and, once introduced into the apparatus, are removed with difficulty. Other gases in order of their effect in destroying these ions are oxygen, hydrogen sulphide, ammonia, methane, ether, and carbon dioxide, the former being about forty times as effective as the latter. Naphthalene and camphor as saturated vapours exerted little effect, but phosphorus reduced the mobility considerably. Hydrogen had a very small effect, which was variable, depending on the method of purification. Thus it was found that ionised hydrogen, specially purified by passage through charcoal cooled in liquid air, also showed the presence of very mobile negative ions. Four kinds were recognised, with mobilities 9·4, 18·9, 28·1, and 170, the latter being probably electrons. The normal negative ion has the mobility 7·4. These ions appear in different proportions in different cases, and only in gas purified with great care.

F. S.

The Ionisation of Hydrogen by *X*-Rays. GEORGE SHEARER (*Phil. Mag.*, 1915, [vi], **30**, 644—658).—The first observers obtained highly divergent values, ranging from 0·026 to 0·5, for the ratio of the ionisation produced by *X*-rays in hydrogen and in air, due, not only to the widely different types of rays employed, but also to the type of ionisation chamber used. Crowther (A., 1909, ii, 287) showed that, as the penetrating power increased, the ratio increased from 0·01 to 0·18, and his results suggest that there was an impurity in the gas the characteristic radiation of which was excited, producing a sudden increase of ionisation, as a certain penetrating power was passed. Beatty, who used homogeneous secondary *X*-radiation of iron, copper, zinc, arsenic, and tin, and a method which entirely eliminated the effect of the walls of the ionisation chamber, found the ratio was constant at 0·0057 for the first four rays, and increased suddenly for the tin ray to 0·04 (*Phil. Mag.*, 1910, [vi], **20**, 320; *Proc. Roy. Soc.*, 1911, [*A*], **85**, 578; A., 1911, ii, 245). This result suggested the presence of a trace of hydrogen arsenide in the hydrogen employed, about 1 part in 6000, and experiments with hydrogen selenide, which should behave in the same way to *X*-rays, showed that it gave an ionisation curve similar to hydrogen. Using Beatty's method, and working over a range of from 1—2 atmospheres, the better to eliminate the effects of the walls, the results were repeated with very carefully purified hydrogen, using tin and copper *X*-rays. The ratio of ionisation in hydrogen to that in air was found to be very small and variable, 0·0018 (Cu) and 0·0035 (Sn) as the mean. One part in 40,000 of hydrogen arsenide would account for the observed ionisation, and in consequence the values given are to be regarded as upper limits rather than the real ratio. The earlier results are probably spurious, and there is no conclusive evidence that the

relative ionisation of hydrogen increases with a decrease in the wave-length of the X-rays. The results are discussed from the point of view of Bohr's model of the hydrogen atom. The greatest possible frequency of this atom is $3{\cdot}26 \times 10^{15}$, one six-hundredth of the frequency of copper rays and one two-thousandth of that of tin rays. The ionisation potential of hydrogen, 11 volts, corresponds also with the frequency 3×10^{15}. From this point of view, hydrogen is not so anomalous as appears at first sight, for its characteristic radiation has a wave-length 1/600 (Cu) or 1/2000 (Sn) of the exciting ray, whereas that of air is 1/50 of that of tin, and nearer tin than hydrogen. This great difference between the wave-length of the exciting and characteristic radiation accounts for the smallness of the observed ionisation on Bohr's model, containing only one electron in the atom. F. S.

Emission of Corpuscles During Chemical Reactions. I. S. TANATAR and E. BURKSER (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 956—958).—The apparatus employed consisted of an electroscope with aluminium leaves, which in most cases were charged positively to about 200 volts. By means of a scale and mirror, the rate of discharge was measured, first in presence of the substances to be used in the reaction, and subsequently during the reaction.

(1) Reactions in which no gases are evolved: with the neutralisation of concentrated sodium hydroxide solution by concentrated sulphuric acid, the oxidation of concentrated sodium sulphite solution by permanganate, and the oxidation of alcohol by potassium dichromate and sulphuric acid, no ionisation was observed. With potassium ferrocyanide and hydrogen peroxide, or ammonia and nitric acid vapours, or ammonia and carbon dioxide, feeble ionisation occurred, and with ammonia and sulphur dioxide marked ionisation. With ammonia and hydrogen chloride, evolved from their concentrated solutions placed on the bottom of the containing cylinder, the ionisation was intense, the dispersion of the charge proceeding at the rate of 10 volts per minute, and the effect being observable more than an hour after the introduction of the solutions; when the electroscope was charged negatively, the ionisation was considerably less marked.

(2) Reactions in which gases are evolved: no ionisation is observed with sulphuric acid and sodium carbonate or sulphite solution, quinol and a mixture of sulphuric acid and permanganate, or concentrated solutions of sodium hydroxide and ammonium chloride. Ionisation occurs with the reactions between sodium amalgam and water, and between potassium ferricyanide and barium peroxide (1 volt per minute). The ionisation is more marked with formic acid and sulphurous acid, calcium and water, and during the first three to five minutes, during which the sodium acts on the water present, with sodium and 96% alcohol. Intense ionisation occurs in the following reactions: the combustion of sulphur; dilute sulphuric acid and zinc, 10 volts per minute, but somewhat less with a negative charge; dilute sulphuric acid and magnesium, 20 volts per minute; zinc dust and hydrogen peroxide

solution, 20 volts per minute; addition of water to calcium carbide, 10 volts per minute, but less when the carbide is dropped below the surface of the water; potassium nitrite and ammonium chloride, 20 volts per minute; sodium hydroxide solution and aluminium, 20 volts per minute; decomposition of ammonium dichromate on a heated quartz dish, 25—30 volts per minute.

With discontinuance or retardation of the reaction, the ionisation also exhibits weakening, which is at first rapid, but proceeds more and more slowly, and in some cases, such as the decomposition of ammonium dichromate, occupies more than an hour. With mineral waters and the gases evolved from them it is, therefore, advisable to determine the radioactivity four to five hours after the sample is taken, since the emanation would then be in equilibrium with its decomposition products, and any reaction between the gases and the salts of the water or the walls of the vessel at an end. The results show also that no relationship exists between the evolution of gases and ionisation. T. H. P.

Production of Helium from Radioactive Substances. A. DEBIERNE (*Ann. Physique*, 1914, [ix], **2**, 423—477).—The technique in the measurement of small quantities of helium has been so advanced that 0·01 mm.^{3} can be measured with precision, and probably one-thousandth of this detected spectroscopically. The method adopted of separation, purification, and measurement of small quantities of helium is described in detail. The measurement of the rate of production of helium, 0·45 mm.^{3} per year, from a particular actinium preparation is described. The ratio between the volume of gas resulting from the decomposition of water and the volume of helium generated is twice as great for actinium as for radium, due, probably, to the greater portion of the α-particles in the latter case being liberated in the gaseous phase. An unexplained emission of a continuous spectrum from the tubes used to detect the helium from actinium in certain circumstances is described.

The rate of formation of helium from polonium has been measured with every possible care, in course of a research on this substance with Mme. Curie. At the same time, the number of α-particles expelled from the polonium has been determined both by the scintillation and electrical counting methods. The result, that 0·578 mm.^{3} of helium was produced in 587 days from a preparation of polonium initially emitting $5·99 \times 10^{10}$ α-particles per minute, leads directly to the value $6·5 \times 10^{23}$ for Avogadro's constant (number of molecules per gram-molecule), and to the value $4·46 \times 10^{-10}$ *E.S.U.* for the atomic charge, which are intermediate between those obtained by Perrin on the one hand, and by Rutherford, Geiger, and Millikan on the other. Incidentally, some other points in connexion with this research on polonium are mentioned. In the spectrum, a line, 4170·5, is considered to be characteristic of polonium, and has been twice observed, in the first case disappearing completely after a lapse of two years, whilst the strength of the lead lines had augmented. Many difficulties have been

encountered, and a new set of experiments on these points is being carried out. F. S.

Production of Helium. A. Debierne (*Ann. Physique*, 1914, [ix], **2**, 478—488).—A number of "blank" experiments made during the work on the production of helium from radioactive substances are described. Certain minerals, such as the fluorspars, have been examined to see if helium is present, and if it is re-formed after expulsion. Helium was found in all specimens of fluorspar in varying degree, which is easily explained, even in absence of all present radioactivity, by the entrainment, during its formation, of radium or other short-lived radio-element; but after removal by heating and recoloration by exposure to the penetrating rays of radium for some months, no more helium could be extracted. In 20 litres of detonating gas no helium was detected, and for the products of the decomposition of water, by the penetrating rays of radium, the result was also negative. The same result was obtained from the gas extracted from mercury lamps and Crookes' tubes. F. S.

A Comparison of Radium Standard Solutions. J. Moran (*Phil. Mag.*, 1915, [vi], **30**, 660—664).—The two liquid Rutherford-Boltwood solution standards of radium, used in determinations of the amounts of radium in rocks, water, and air by various investigators, have been compared with a liquid standard prepared at Washington from radium checked by γ-rays against the International solid standard. The two standards were originally of strengths 100 : 1, and agreed closely still, but on continued boiling and testing a regular decline in value was observed in every solution examined. An old standard repeated, used by Eve in 1908, showed only 45% of its original content of radium as compared with the new Washington standard. Old solutions are not trustworthy, and a new one should be used for each set of experiments. On adding more hydrochloric acid, a deteriorated standard is more or less regenerated. The ratio of the strong standard to the Washington standard was 96%, and of the weak standard 98%. F. S.

The Relation Between Uranium and Radium. VI. The Life-period of Ionium. Frederick Soddy and Miss Ada F. R. Hitchins (*Phil. Mag.*, 1915, [vi], **30**, 209—219. Compare A., 1910, ii, 921).—The measurements on the growth of radium in four uranium preparations, purified during the years 1905—1909, and containing from 0·255 to 3·0 kilos. of uranium (element), have shown of late a clear increase in the rate of growth of radium in the largest preparation, purified in 1909. The curve, quantity of radium present plotted against time, agrees with the theoretical curve deduced from the assumption that ionium is the only long-lived intermediate product between uranium and radium, and that its period of average life is 100,000 years. The next largest preparation, 0·408 kilo. of uranium, purified in 1906, also shows a

distinct increase in the rate of growth, and the period of ionium, calculated from the curve, agrees with that stated, although the quantities of radium involved are too small to be sure of. There is now, for the first time, direct experimental evidence that uranium produces radium, and of the period of ionium. The estimate of 100,000 years is probably not far from the true period.

F. S.

Electrical Conductivity of Aqueous Hydrochloric Acid, Saturated with Sodium Chloride, and a New Form of Conductivity Cell. F. D. MILES (*Proc. Roy. Soc. Edin.*, 1915, **35**, 138—145).—A conductivity cell is described which is specially suitable for the measurement of solutions which are saturated with a solid or contain a volatile constituent, either solvent or dissolved substance. Using this cell, determinations have been made of the specific conductivity of a series of solutions of hydrogen chloride containing from 16 to 27% of hydrogen chloride, and also saturated with sodium chloride at 18°. The percentage composition by weight of the various mixtures has also been accurately determined. Within the above-mentioned range of concentrations, the saturated salt-acid solution has a lower specific conductivity than the aqueous solution of hydrogen chloride alone from which it is derived. Of the salt-saturated acid solutions, that one has the maximum conductivity which could be prepared by adding salt to hydrochloric acid containing 21·9% of hydrogen chloride. Of solutions of hydrogen chloride alone in water, that containing 19·1% of hydrogen chloride has the maximum conductivity. The critical concentration of hydrogen chloride at which hydrochloric acid is able to affect the colour of cobalt chloride is changed, in the same sense as the concentration of hydrogen chloride is changed by saturating with sodium chloride, thus confirming the hypothesis of Gibson (A., 1912, ii, 726) that homogeneous chemical systems, in which a reaction occurs either spontaneously or under the influence of light, are transformed in such a way that the specific conductivity is increased, unless this tendency is opposed by stronger chemical affinities.

J. F. S.

Dissociation of Water in Salt Solutions. WILH. PALMAER and K. MELANDER (*Zeitsch. Elektrochem.*, 1915, **21**, 418—425).—For the purpose of obtaining more information about the complete electrical conductivity curve of a mixture of two substances, a series of measurements have been carried out to determine the concentration of hydrogen ions in concentrated salt solutions, the reason for these determinations being that in very concentrated solutions the water is to be regarded as the dissolved substance. In the present paper, solutions of lithium chloride and calcium chloride are considered, and the concentrations are so chosen that liquid contact potentials can be regarded as non-existent, or at most of negligible size. The measurements consisted in determining the potential difference between two hydrogen electrodes immersed in the given solutions, the cells measured being constituted thus:

Pt,H_2,conc. solution | dil. solution H_2,Pt, the dilute solution being the negative electrode in all cases. The measurements with lithium chloride were made at 22°, and the concentrated solution was 11·8*N* in all cases; the dilute solution was varied from pure water to 1·5*N*, 1·8*N*, 3·0*N*, 5·7*N*, and 7·2*N*. With calcium chloride, the measurements were made at 25·5°, with 10·0*N* as the concentrated solution, and 0·65*N*, 1·50*N*, 2·18*N*, 2·50*N*, 4·00*N*, and 5·07*N* as the dilute solution. By means of a kinetic consideration, it is shown that the potential difference between two solutions of the same ions with different concentrations is equal to zero when the ion pressure is the same in both solutions. It is shown from the measurements that 11·8*N*-solution of lithium chloride contains 240 times as many hydrogen ions as a 1·5*N*-solution of lithium chloride, and a 10·0*N*-solution of calcium chloride contains 235 times as many hydrogen ions as a 1·7*N*-solution of calcium chloride. These values are, however, only to be regarded as approximately correct. J. F. S.

Temperature-coefficient of Conductivity in Alcoholic Solutions and Extension of Kohlrausch's Hypothesis to Alcoholic Solutions. Devendra Nath Bhattacharyya and Nilratan Dhar (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 373—374).—According to measurements of the electrical conductivity of the sodium salts of various acids in ethyl-alcoholic solutions at temperatures between 0° and 30°, the temperature-coefficient is about 0·024. This is the value of the temperature-coefficient of the fluidity of ethyl alcohol. The identity is supposed to show that the ions are surrounded by an envelope of alcohol molecules.
H. M. D.

Alcoholic Solutions of Cadmium Iodide. Frederick H. Getman and Vernette L. Gibbons (*J. Amer. Chem. Soc.*, 1915, **37**, 1990—1996).—The values obtained for the conductivity of solutions of cadmium iodide in methyl alcohol by Zelinsky and Krapiwin (A., 1897, ii, 5), and Jones and Carroll (A., 1905, ii, 73), show considerable divergence. The latter authors also measured the conductivity of solutions of cadmium iodide in ethyl alcohol. The conductivity of the salt in both solvents has now been redetermined at 25°.

The conductivity curves present certain abnormalities which resemble those observed in the case of certain non-aqueous solutions of silver nitrate (Gibbons and Getman, A., 1914, ii, 704), and are explained in the same way, as due to the existence in the solutions of complexes formed by the combination of the solvent and the solute.

The densities and refractive indices of the solutions of various concentrations have been determined at 20·5°, and it has been found that each is a rectilinear function of the concentration. The specific refraction was practically constant for the more concentrated solutions in methyl alcohol, but for the less concentrated solutions, the value increased rapidly with dilution. The specific

refraction of the solutions in ethyl alcohol was not constant at any point, and diminished rapidly with dilution. The variations in the specific refraction of these two classes of solutions run parallel to the variations in the conductivity curves for the same solutions, and it is therefore evident that there is a close relationship between conductivity and specific refraction. E. G.

Electrical Conductivity and Dissociation in Solvents with Dielectric Constants up to 13. A. N. Sachanov and J. S. Prsheborovski (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 849—859. Compare A., 1913, ii, 283, 822; 1914, ii, 92).—The investigations here described were carried out with a view to determine the change in form of electrical conductivity curves, especially as regards the displacement of the minimum, as the dielectric constant of the solvent increases from a small value to a high one like that of water. Use was made of silver nitrate as the normal electrolyte, and of the following solvents, the dielectric constants of which are given in brackets: aniline (6·85), mixture I of aniline and pyridine (8·0), quinoline (8·9), mixture II of aniline and pyridine (9·7), and pyridine (12·56). With the exception of quinoline, which dissolves only about 0·5 gram-mol. per litre, these solvents readily dissolve silver nitrate. With the more concentrated solutions, measurements were also made of the viscosity, the value which the molecular conductivity would have if the viscosity of the solution were equal to that of the solvent being calculated by means of the formula $M=\mu.\eta/\eta_0$, where μ is the observed molecular conductivity and η and η_0 the viscosities of the solution and pure solvent respectively. With highly concentrated and excessively viscous solutions, such correction is only approximately correct, since, in these cases, the mobility of the ions may not be in direct proportion to the viscosity of the solution (compare Washburn, A., 1911, ii, 862). All the measurements were made at $25\pm0·05°$.

The results obtained indicate the importance of the correction for viscosity on the characteristics of electrolytic dissociation in solvents, the dielectric constants of which are not too small (9—12). Only with aniline and with mixture I of aniline and pyridine, that is, where the dielectric constant does not exceed 8, does the curve of molecular conductivity exhibit a distinct minimum; the correction for viscosity merely increases the rate at which the molecular conductivity augments with the concentration. In mixture II of aniline and pyridine, and in quinoline, the formation of a minimum is scarcely discernible, the curve showing only a bend; in these cases, the viscosity correction completely changes the appearance of the curve, anomalous electrolytic dissociation being clearly expressed in the concentrated solutions. With pyridine solutions, the molecular conductivity curve exhibits normal character, but the viscosity corrections reveal marked abnormality in the electrolytic dissociation.

The general character of the curves is in accord with the deductions previously made (*loc. cit.*), anomalous dissociation becoming

more rare as the dielectric constant of the solvent diminishes. Walden (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 1091) has shown that the position of the minimal molecular conductivity is related to the dielectric constant of the solvent, ϵ, according to the expression $\epsilon\sqrt[3]{V}=$ a constant for a given electrolyte, V being the dilution corresponding with this minimum. The author's results show that agreement with this relation is obtained only when the molecular conductivity is corrected for the viscosity.

Walden (*loc. cit.*) found that, with many electrolytes, the maximal molecular conductivities occur at dilutions of about 1 litre, and this author laid it down as a general rule that, independently of the characters of the electrolyte and solvent, this maximum is exhibited by solutions of normal, or approximately normal, concentration. The author's results, and those obtained for solutions of silver nitrate in amylamine by Kahlenberg and Ruhoff (A., 1903, ii, 464), and in methylamine by Franklin and Gibbs (A., 1907, ii, 840), show, however, that the dilutions corresponding with the maximal molecular conductivities vary within wide limits, and are closely related to the dielectric constants of the solvents; these dilutions are: for amylamine ($\epsilon=4{\cdot}5$), 1·0; aniline, 1·5; mixture I of aniline and pyridine, 3·6; quinoline, 7·0; mixture II of aniline and pyridine, 4—8; and methylamine ($\epsilon=10$), 2 litres. The maximal molecular conductivities of silver nitrate in these solvents disappear when the corrections for viscosity are introduced, the curves then rising uninterruptedly as the concentration increases. The appearance of maximal molecular conductivities is, therefore, a consequence of the excessive increase of the viscosities of the solutions with their concentrations, such increase overcompensating the simultaneous increase in the dissociation of the electrolytes. This phenomenon is exhibited by all binary, strongly dissociated electrolytes (A., 1914, ii, 92, 419). In pyridine, and also in solvents with still higher dielectric constants, strongly dissociated electrolytes show no maximal molecular conductivity, but weaker electrolytes often give maxima in such solvents.

The viscosity of solutions of silver nitrate in the solvents employed increases very rapidly with the concentration. This behaviour is general with all electrolytes in solvents with low dielectric constants, which thus differ sharply from water, the latter being the typical solvent with a high dielectric constant. Aqueous solutions of some salts increase slightly, whilst those of others even diminish, in viscosity as the concentration increases. T. H. P.

Electrical Conductivity and Dissociation in Solvents with Dielectric Capacities of 13—80. A. N. Sachanov and A. I. Rabinovitsch (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 859—870. Compare preceding abstract).—The electrical conductivity of silver nitrate has been studied at $25\pm0{\cdot}05°$ in the following solvents of high dielectric capacities: *m*-chloroaniline, 13·35; a mixture of pyridine (2 vols.) with acetonitrile (1 vol.), 19·7; acetonitrile, 35·8; a mixture of acetonitrile (1 vol.) with water (1 vol.), 59·7; and

water, 81·0. In all cases, the molecular conductivity diminishes uninterruptedly with the concentration. When, however, corrections are introduced for the changes in viscosity, which are very considerable at high concentrations, the molecular conductivity exhibits in all cases a minimum, this being particularly sharp for *m*-chloroaniline and the mixture of pyridine and acetonitrile. For the above solvents, and for those previously investigated, the dilutions at which the minimal molecular conductivities of silver nitrate occur are as follows, the numbers in brackets indicating the dielectric capacities: benzylamine, greater than 80 litres (5·2); aniline, 80 (6·85); mixture I of aniline and pyridine, 50 (8·0); quinoline, 45 (8·9); mixture II of aniline and pyridine, 35 (9·7); pyridine, 15 (12·56); *m*-chloroaniline, 12; pyridine (2 vols.) + acetonitrile, 3; acetonitrile, 1; acetonitrile (1 vol.) + water (1 vol.), 0·7; water, 0·2.

Walden's equation, $\epsilon \sqrt[3]{V_m} = \text{const.}$, where ϵ is the dielectric capacity of the solvent and V_m the dilution at the minimum molecular conductivity, gives satisfactorily constant values, namely, 30·6, 28·4, and 35·4, for *m*-chloroaniline, pyridine + acetonitrile, and acetonitrile respectively. With acetonitrile + water and water the values 53·0 and 47·4 are obtained, the deviations from constancy in these cases being probably due to the approximate character of the corrections for viscosity and to inaccuracy in the determination of the position of minimum conductivity when this occurs at very high concentrations.

The regular, continuous displacement of the minimal conductivity in the direction of greater concentration as the dielectric capacity of the solvent increases leads to the conclusion that, in all solvents, the minimum molecular conductivity and the gradual increase of the latter with the concentration are conditioned by one and the same cause. If anomalous dissociation is due to the formation of complexes which readily decompose into ions, it is natural that in solvents of high dielectric capacities the formation of such complexes should take place only in very concentrated solutions.

The curves representing the viscosities of the solutions as ordinates in relation to the dilutions as abscissæ are of characteristic form, and bear a general resemblance to those of anomalous molecular conductivity. In order to render comparable the viscosity-dilution curves for the different solvents for which $\epsilon = 6{\cdot}85$—81, the values of $\eta : \eta_0$, the ratio of the viscosity of the solution to that of the pure solvent, are taken as ordinates. The magnitude of the coefficient, $(d\eta/\eta_0)/dV$, depends on the nature of the solvent, the increase of the viscosity with the concentration being determined principally by two factors, namely, the dielectric constant and the molecular volume of the solvent.

The results of the present and earlier papers (compare A., 1914, ii, 92, 419) lead to an important conclusion of fundamental significance for the whole theory of electrolytic dissociation. The molecular electrical conductivities of aqueous solutions of electrolytes diminish continuously with the concentration to a limiting value

approximating to zero. The same holds for the electrolytic dissociation of dissolved salts, this being proportional to the molecular conductivities. On this foundation is based the common view that, on dissolution, salts undergo decomposition into ions, that is, that salts as such are non-dissociated. The data now obtained, however, show clearly that the uninterrupted diminution of the molecular conductivity in concentrated solutions as the concentration of the electrolyte increases is the result of the obscuration of the actual course of the phenomenon by the excessive augmentation of the viscosity in such solutions. When corrections are introduced for the increase in viscosity, it is found that the molecular conductivity passes through a minimum, and subsequently increases, as the concentration is raised. Consequently, with concentration of its solution, the electrolytic dissociation of a salt tends towards a limiting value, which is not zero, but has a definite magnitude. It follows, then, that when the proportion of solvent becomes zero, the individual salt should be dissociated into ions. The extent of such dissociation for silver nitrate and other individual salts is probably of the same order as that of their aqueous solutions of medium concentration. The process of dissolution merely alters the existing dissociation of the salt in one or the other direction, according to the dielectric properties of the solvent and to the change in the electric solution pressure of the ions, which may induce the process of solution or solvatation. T. H. P.

Influence of Electrolytes on the Dissociating Power of a Solvent. II. A. N. Sachanov and P. I. Gontscharov (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1244—1260. Compare A., 1914, ii, 419).—Electrometric investigation of the dissociation of silver nitrate in presence of increasing proportions of ammonium nitrate or potassium or lithium chlorate shows that the concentration of the silver ions falls continuously as the concentration of the "neutral" salt increases, this result being in disagreement with the hypothesis of the dissociating influence of ions. Similar investigation of normal hydrogen cells shows that the absolute magnitude of the potential of the hydrogen electrode in solutions of acetic or hydrochloric acid diminishes on addition of "neutral" salts to the acid solutions, the influence of salts which combine with avidity with water being especially marked. The view that "neutral" salts increase the dissociation of acids, producing diminution in the absolute magnitude of the potential of the hydrogen electrode, is untenable, as it leads to degrees of dissociation of acids exceeding unity. This result is in agreement with that obtained by means of conductivity measurements of mixtures of electrolytes in aqueous solution (*loc. cit.*) (compare Poma and Patroni, A., 1914, ii, 440). The view is expressed that the electrolytic solution pressure of hydrogen depends on a process of hydration of the hydrogen ions. T. H. P.

Potential of the Rubidium Electrode. Gilbert N. Lewis and William L. Argo (*J. Amer. Chem. Soc.*, 1915, **37**, 1983—1990).—The potential of the rubidium electrode has been determined by a

similar method to that employed in the case of the sodium, potassium, and lithium electrodes (A., 1910, ii, 1027; 1912, ii, 225; 1913, ii, 467). The results show that the potential of rubidium in a *N*-solution of rubidium ions at 25° is 3·205 volts, against the normal calomel electrode taken as zero. This value was secured by combining (1) 2·1308 volts, the normal electrode potential of rubidium amalgam, obtained from measurements of the potential of the amalgam in a 0·1*N*-aqueous solution of rubidium hydroxide against the normal calomel electrode, with (2) 1·0745 volts, the difference of potential between rubidium and rubidium amalgam in a solution of rubidium iodide in a mixture of ethylamine and ammonia.

The potentials of the alkali metals decrease in the order lithium, rubidium, potassium, sodium, which corresponds with the order of the heats of formation of the ions of the respective metals in aqueous solution. E. G.

Anodic Potentials of Silver. I. The Determination of the Reaction Potentials of Silver and their Significance. John Henry Reedy (*Amer. J. Sci.*, 1915, [iv], **40**, 281—298).—The potential at which silver, as anode, reacts with various solutions has been determined in a large number of cases. The method consisted in placing a silver anode and a platinum cathode in a vessel containing the solution and impressing a steadily increasing potential on the electrodes, and measuring the current which passes at each voltage. Simultaneously, the potential difference between the anode and a comparison electrode was determined by the compensation method. The comparison electrode was

$$Hg,Hg_2SO_4,NH_2SO_4$$

($PD = +0·679$ volt) for the acid solutions and $Hg,HgO,NNaOH$ ($PD = +0·112$ volt) for alkaline solutions. The author uses the term "reaction potential" to designate that potential at which a reaction just begins, and includes in it deposition potential, solution potential, and oxidation potential. The following potential differences were obtained in the case of the electrolytes mentioned: *N*-sulphuric acid, 0·521 volt; *N*-sodium sulphate, 0·523 volt; *N*/2-potassium sulphate, 0·521 volt; *N*-zinc sulphate, 0·521 volt; *N*-magnesium sulphate, 0·522 volt; *N*-copper sulphate, 0·550 volt; 0·0032*N*-mercurous sulphate, 0·660 volt; *N*-nitric acid, 0·520 volt; *N*-potassium nitrate, 0·521 volt; *N*-sodium nitrate, 0·520 volt; *N*-phosphoric acid, 0·521 volt; *N*-disodium hydrogen phosphate, 0·523 volt; *N*-oxalic acid, 0·520 volt; *N*-ammonium oxalate, 0·521 volt; *N*-acetic acid, 0·522 volt; *N*-potassium chloride in *N*-sulphuric acid, 0·222 volt; *N*-potassium bromide in *N*-sulphuric acid, 0·077 volt; *N*-potassium iodide in *N*-sulphuric acid, −0·152 volt; *N*-sodium hydroxide, 0·346 volt; *N*-potassium hydroxide, 0·348 volt; *N*-sodium thiosulphate, −0·147 volt; *ca.N*-potassium cyanide, −0·611 volt. In all those cases where the reaction potential is about 0·521 volt it is shown that concentration has no influence on the potential, and this value is regarded as the ionisation potential of silver. Reaction potentials smaller than 0·521

volt appear in those cases where the silver compound formed is insoluble or contains the silver largely in the form of complex ions. These deposition potentials, except in the region of the solution potential of silver, are logarithmic functions of the dilution, as is to be expected from the Nernst formula for *E.M.F.* values. Generally, however, the increase in the reaction potential with dilution was found to be somewhat greater than would be expected from theoretical considerations. Certain electrolytes were made to show two reaction potentials (for example, potassium iodide in sulphuric acid), the lower one being due to the deposition of the anion, and the other (0·521 volt) due to the solution of the silver. Electrodes coated with insoluble silver compounds corresponding with the anion of the solution show higher deposition potentials than do electrodes of bright silver. As a rule, the presence of cations of other metals was found to have no effect on the reaction potentials of silver. In the case of the cations copper and mercury, however, silver shows abnormally high solution potentials. It is suggested that these metals may form solid solutions with silver, with a resultant lowering of its solution pressure. The author has determined the solubility of silver oxide, silver chloride, silver bromide, and silver iodide by plotting the reaction potentials of solutions of the alkali compounds of the anions against the dilution, and on the same graph plotting the potential $Ag \rightleftarrows Ag^{\cdot}$ for the same dilutions. The points of intersection give the concentration of $Ag^{\cdot}$ ion which must be in solution at the electrode and in equilibrium with the electrode. Hence, since at such high dilutions the salts can be regarded as completely ionised, the solubility follows. The values obtained are $Ag_2O = 0{\cdot}6 \times 10^{-4}$, $AgCl = 1{\cdot}4 \times 10^{-5}$, $AgBr = 7{\cdot}0 \times 10^{-7}$, and $AgI = 1{\cdot}0 \times 10^{-8}$. These values agree very well with the values obtained by the *E.M.F.* method and the conductivity method. J. F. S.

Liquid Junction Potentials. Duncan A. MacInnes (*J. Amer. Chem. Soc.*, 1915, **37**, 2301—2307).—A theoretical paper in which it is shown that the probable value of the potential E_L of the liquid junction connecting solutions of different concentrations of the same salt may be expressed by the equations $E_L = E(2n_c - 1)/2$ and $E_L = E_t(1 - 1/2n_c)$, in which E is the voltage of a concentration cell without transference and E_t that of the concentration cell with transference, each of these cells containing the solutions which are in contact at the liquid junction. By combining junctions to which these equations apply with junctions the voltage of which may be computed by Lewis and Sargent's formula (A., 1909, ii, 369), the potential between any two univalent salt solutions may be calculated to a few tenths of a millivolt. E. G.

The Reaction between Gas and Pole in the Electrical Ignition of Gaseous Mixtures. W. M. Thornton (*Proc. Roy. Soc.*, 1915, [*A*], **92**, 9—22. Compare A., 1914, ii, 524, 834).—The smallest current which is capable of igniting mixtures of ethane and air, and also carbon monoxide and air, has been determined

by experiments with break-sparks produced between aluminium, iron, nickel, copper, and platinum points by the use of both continuous and alternating currents. The nature of the metal poles is found to have considerable influence on the magnitude of the least igniting current. In the use of continuous-current break-sparks, the difficulty of ignition increases with the density of the metal. When alternating current or condenser discharge sparks are employed, the ignition seems to depend on the rate at which the poles reach a condition in which discharge takes place, and is therefore influenced by the density, specific heat, and thermal conductivity.

The influence of the metal on the least igniting current was also investigated by observations on mixtures of air and coal-gas in which long, disruptive discharge sparks were used. In this case, the tenacity of the metal appears to be of the greatest importance. When carbon poles are employed, these long, disruptive sparks have the greatest effect on the methane, whereas the hydrogen is chiefly affected by condenser discharge sparks. H. M. D.

The Silent Discharge in Gases at Atmospheric Pressure. St. Sachs (*Ann. Physik*, 1915, [iv], **47**, 886—926).—According to Warburg's theory (*Verh. Deut. Physikal. Ges.*, 1903, **20**, 382) of the action of the Siemens ozoniser, the apparatus behaves as an ordinary condenser until the applied potential difference exceeds a certain limiting value. Above this limit discharge occurs, and electricity must be supplied to maintain the potential difference constant. The ratio of this quantity of electricity to the difference of potential affords a measure of the "apparent capacity" of the ozoniser.

The apparent capacity of an ozoniser has been investigated in a series of experiments with air, oxygen, nitrogen, hydrogen, carbon dioxide, and mixtures of helium and neon at atmospheric pressure. It is found that the apparent capacity of the ozoniser, through which hydrogen or nitrogen is passed, is independent of the rate at which the gas is passed through the apparatus. On the other hand, the experiments with air, oxygen, and carbon dioxide show that the apparent capacity increases with the rate at which the gas is passed through the ozoniser. Chemical changes are brought about by the action of the silent discharge on these three gases, whereas these changes are absent in the case of hydrogen and nitrogen.

The observations lead to the conclusion that chemical reactions facilitate the passage of the discharge, but that the accumulation of the products of the reactions is, in general, unfavourable to the discharge. The fact that the apparent capacity of the ozoniser when supplied with air, oxygen, or carbon dioxide varies with the speed of the current of gas is obviously in agreement with this statement. H. M. D.

Thermoelectric Properties of Carbon. William C. Moore (*J. Amer. Chem. Soc.*, 1915, **37**, 2032—2037).—An investigation of

the thermoelectric properties of commercial arc carbons has been carried out with a view to elucidating the nature of so-called amorphous carbon. Six pieces of carbon were used, two of which were of the same kind. One piece was clamped against each of the others in turn, and the free ends were connected through a circuit containing a millivoltmeter as a galvanometer. On heating the clamped end, a considerable *E.M.F.* was developed in the case of every couple except that formed of two carbons of the same kind. A similar study was made of carbon–copper couples.

The results afford evidence that amorphous carbon is not a single, definite substance. The thermoelectric properties vary with the temperature, and depend on the raw material used for making the carbon and the treatment accorded to it during the process of manufacture. Some varieties of arc carbons give a constant *E.M.F.* over a considerable range of temperature, indicating the possibility of a transition interval for such carbons. E. G.

The Thermoelectric Properties of Special Steels. Eugene L. Dupuy and Albert M. Portevin (*J. Iron Steel Inst.*, 1915, **91**, 306—335).—The thermoelectric force has been measured against pure copper and lead for the ranges −78° to 0° and 0° to 100°. The method lends itself to the determination of the constitution of the steels, those which consist of solid solutions giving continuous curves, falling very rapidly at first, when the *E.M.F.* is plotted against the percentage of added metal. On the other hand, steels which contain "double carbides," such as chromium, tungsten, and molybdenum steels, give curves which fall, then rise, and then remain horizontal or again fall. C. H. D.

Phenomenon of Passivity in Connexion with Ferrous Alloys of Different Composition and Structure. Hal Walters Moseley (*J. Amer. Chem. Soc.*, 1915, **37**, 2326—2333).—The experiments described in this paper were carried out with a number of different samples of iron and steel of known composition and structure in order to compare their behaviour under conditions which induce passivity. A comparative study of the transition points from active to passive when the samples were employed as anodes in different electrolytes has shown that the transition density is not related in any simple way to the composition and structure of the metal. It is considered that there is not an instantaneous change from the active to the passive state, but that a gradual adjustment takes place towards a new condition of equilibrium, since, in general, less iron enters solution as the current density required for passivifying is approached. The current density necessary increases with the electrode potential. As a rule, metals with low solution tension become passive at a lower current density than those with high solution tension. E. G.

Velocity of Ions at 0°. Devendra Nath Bhattacharyya and Nilratan Dhar (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 375—384).—The electrical conductivity of dilute aqueous solutions

of various electrolytes has been measured at 0°, and, by extrapolation, values representing Λ_∞ have been obtained. By combining these data with the transport ratios for very dilute solutions at 0° (Noyes and Falk, A., 1911, ii, 861), the authors have obtained the following values for the ionic mobilities at 0°: $H^{\cdot}$, 223·9; $NH_4^{\cdot}$, 39·2; $Li^{\cdot}$, 19·3; $Na^{\cdot}$, 25·6; $K^{\cdot}$, 42·1; $\frac{1}{2}Ca^{\cdot\cdot}$, 29·5; $\frac{1}{2}Sr^{\cdot\cdot}$, 31·7; $\frac{1}{2}Mg^{\cdot\cdot}$, 25·8; Cl', 40·8; Br', 41·7; NO_3', 41·3; $\frac{1}{2}SO_4''$, 42·6.

H. M. D.

Some Cases of Ionisation of [Electrolytes into the Two Complex Ions]. C. Blomberg (*Zeitsch. Elektrochem.*, 1915, **21**, 437—439).—A theoretical paper in which it is shown that the conductivity of solutions of salts which contain few or no simple ions is due to the presence of two complex ions. The ionisation of such substances is assumed to take place according to the scheme $2AB = A_2B^{\cdot} + AB_2'$, that is, a single molecule is supposed to ionise in the ordinary way, and then each single ion combines with an undissociated molecule to form a complex ion. Among the substances as to which the author advances evidence for the complexity of their ions, are: magnesium citrate, calcium citrate, ferric pyrophosphate, lead acetate, many soluble basic salts, cadmium sulphate, and copper sulphate. The ionisation in the last-mentioned case is represented by $3CuSO_4 \rightleftarrows Cu_2SO_4^{\cdot\cdot} + Cu(SO_4)_2''$, and in the first-mentioned case by $Mg_3Ci_2 \rightleftarrows Mg_2Ci^{\cdot} + MgCi_2'$. The fact that certain electrolytes, such as silver iodide, magnesium citrate, and ferric pyrophosphate, dissolve equally well in solutions of salts of the anion, and also in solutions of salts of the same cation, is explained on the same basis.

J. F. S.

Magnetic Susceptibility and the Number of Magnetons of Nickel in Solutions of Nickel Salts. P. Weiss and (Miss) E. D. Bruins (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 246—254).—According to measurements of the magnetic susceptibility of aqueous solutions of nickel chloride, nitrate and sulphate, it is found that the coefficient of magnetisation of the nickel atom at 20° is independent of the nature of the salt and of the concentration of the solution. The mean value is $445{\cdot}1 \times 10^{-5}$, and the number of magnetons per atom is equal to 16·06.

Ammoniacal solutions of the nickel salts give $419{\cdot}2 \times 10^{-5}$ for the coefficient of magnetisation of the nickel atom, and 15·58 for the number of magnetons per atom.

Within the limits of experimental error, the atomic susceptibility χ_a changes with the temperature in accordance with Curie's law. For neutral or acid solutions $\chi_a T = 1{\cdot}302$, and for ammoniacal solutions $\chi_a T = 1{\cdot}223$.

H. M. D.

Magneto-chemical Researches on Ferrous Salts in Solution. P. Weiss and (Miss) C. A. Frankamp (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 254—258).—The magnetic susceptibility of solutions of ferrous sulphate and ferrous ammonium sulphate of varying concentration has been examined. The data indicate that

the atomic susceptibility of iron is the same for both solutions, and is independent of the concentration. The number of magnetons per atom is equal to 26·5. In very dilute solutions the numbers obtained seem to show that this number varies somewhat, but the anomaly disappears on the addition of sulphuric acid, and is probably due to hydrolysis. H. M. D.

Conduction of Heat in Gases and the Dissociation of Hydrogen into Atoms. Teófilo Isnardi (*Zeitsch. Elektrochem.*, 1915, **21**, 405—417).—Langmuir (A., 1912, ii, 231, 826) has shown that the thermal conductivity of hydrogen increases very rapidly as the temperature approaches 2000°, and from measurements of the conductivity he has calculated the degree of dissociation of hydrogen at these temperatures. The present author shows that this method of calculation leads to the value 148% for the dissociation of hydrogen. In consequence, he has therefore redetermined the conductivity of hydrogen at pressures of 2·5, 5·0, 10·0, and 20·0 cm. of mercury, and at temperatures 1600—3300° absolute. It is shown that the quantity of heat lost from a wire which is surrounded by a dissociated gas can be calculated by means of the Nernst equation. The results obtained by this calculation agree extremely well with the experimental values. From these results, it is shown that the heat of dissociation and the degree of dissociation can be calculated if the value of the thermal conductivity is known. The heat of dissociation, U, is found to be 95,000, with a probable error of 2—3%. The degree of dissociation is calculated by the expression

$$\log(1/\alpha^2-1)=U/RT-\log T+\log P-2\cdot95,$$

the probable error being 10%. Among the values given, the following occur: at 3200° abs. and 25 mm., $\alpha=0\cdot557$; at 3200° abs. and 50 mm., $\alpha=0\cdot511$; at 3100° abs. and 100 mm., $\alpha=0\cdot255$; and at 3100° abs. and 200 mm., $\alpha=0\cdot230$. The results of the present calculations agree within the limits of error with the results deduced from the kinetic theory and with the results obtained from measurements of the specific heat of hydrogen by the explosion method. J. F. S.

Freezing-point Solubility Law for Ideal Solutions. Edward W. Washburn and John W. Read (*Proc. Nat. Acad. Sci.*, 1915, **1**, 191—195).—Solutions of similarly constituted substances in one another, when formed without heat or volume change, constitute ideal solutions. For such solutions, the vapour pressure of a constituent, A, is proportional to the molecular fraction, x_A, that is, $dp_A=dkx_A$. From this law the author deduces the freezing-point solubility law, and shows that for an ideal solution of two substances, A and B, the change in the freezing point caused by an increase in the molecular fraction of each component is given by the equations $dT/dx_A=RT^2/L_Ax_A$ and $dT/dx_B=RT^2/L_Bx_B$, in which T is the absolute temperature of the freezing point and L is the heat of fusion per molecule. At the eutectic point both these equations hold simultaneously, and consequently the eutectic

temperature can be calculated from them. The derived expressions for obtaining this quantity are

$$2{\cdot}303 \log_{10} x_A = -L_A(To_A - T)/RTo_A T,$$
$$2{\cdot}303 \log_{10} x_B = -L_B(To_B - T)/RTo_B . T,$$

in which To_A and To_B are the absolute melting points of the pure substance and T is the eutectic point. These equations have been controlled by the results of experiments with the three binary mixtures formed from the substances benzene, diphenyl, and naphthalene. The eutectic points found were benzene–naphthalene, $-3{\cdot}48°$ ($-3{\cdot}56°$); benzene–diphenyl, $-5{\cdot}8°$ ($-6{\cdot}1°$); naphthalene–diphenyl, 39·4° (39·4°), the values in brackets being those calculated by the above formulæ. The above-mentioned equations represent the most generally applicable freezing point and solubility law, and by means of them the freezing point of a given solution or the solubility of a given solid in a liquid can be calculated if two conditions are fulfilled. These are: (1) the heat of dilution must be practically zero for the range of concentration involved, and (2) the dilution of the solution must not be accompanied by chemical change of any kind. Two general laws follow from the foregoing considerations: (1) When a crystalline substance, A, is dissolved in any solvent, B, with which it forms an ideal solution, its solubility (expressed in terms of its molecular fraction) is entirely independent of the nature of the solvent, B, and is therefore the same in all such solvents. The solubility depends on the melting point, heat of fusion of A, and the temperature, and can be calculated from these data. (2) The principles involved here also furnish a ready and definite method for detecting the presence of racemates in the liquid state.

J. F. S.

Interpretation of Molecular Weight Results from Measurements on Solutions. W. E. S. Turner (*J. Amer. Chem. Soc.*, 1915, **37**, 2063—2064).—Beckmann and Maxim (this vol., ii, 314) have recorded determinations of the molecular weight of phenol, from which they have drawn the conclusions: (1) that in carbon tetrachloride between 75·4° and 54·1°, change of temperature has little effect on the molecular weight, but that at $-23°$ the degree of association is distinctly greater than at 75°; and (2) that change of concentration has a much greater effect on the molecular size than variation of temperature.

It is now pointed out that in interpreting their results, Beckmann and Maxim did not take into account the variation of the dielectric constant of the solvent with the temperature, and it is shown that the results are in harmony with the rule that the higher the dielectric constant of the solvent, the smaller is the degree of association of the solute. E. G.

Isothermals of Diatomic Substances and their Binary Mixtures. XV. Vapour Pressures of Oxygen and Critical Points of Oxygen and Nitrogen. H. Kamerlingh Onnes, C. Dorsman, and G. Holst (*Proc. K, Akad. Wetensch. Amsterdam*, 1915, **18**, 409).—The temperatures recorded in a table giving the vapour

pressures of liquid oxygen (this vol., ii, 142) are found to require small alterations. According to the corrected table, the vapour pressure increases from 9·096 atm. at −154·87° to 49·640 atm. at −118·88°. The corrected critical temperature of oxygen is −118·82°. H. M. D.

[**Vapour Pressures of Water and Certain Organic Liquids and the Relation between Corresponding Boiling Points**]. J. M. Crafts (*J. Chim. Phys.*, 1915, **13**, 105—161. Compare A., 1913, ii, 829).—Measurements have been made of the vapour pressure of water at temperatures between 135° and 230° by a method involving a comparison of the temperatures at which water and naphthalene boil under the same pressure, which was measured by means of a column of mercury. The results are compared with those obtained by Regnault and by Holborn and Henning (*Ann. Physik*, 1908, **26**, 882; 1910, **31**, 968). In general, the boiling points agree fairly closely, although the temperatures recorded by Holborn and Henning are about 0·05° to 0·1° higher than those obtained by the author.

A comparison is made of the corresponding boiling points of a number of substances over a considerable range of pressure, and it is shown that the formula $(t_A - t'_A)/(t_B - t'_B) = q + c(t_B - t'_B)$, in which t_A and t_B, t'_A and t'_B are corresponding boiling points for the substances A and B, and q and c are constants, affords a satisfactory account of the relations between the corresponding boiling points of benzene, aniline, and various aniline derivatives over a wide range of pressures. This formula is compared with the formulæ put forward by Düring and by Ramsay and Shields by reference to the data for a number of different substances. The general conclusion is that none of these formulæ affords a means of representing the boiling-point relations over a very large range of pressure (0·02 to 40 metres of mercury), although they may be quite satisfactory for relatively small ranges.

Tables are given showing (1) the vapour pressure of benzene between −10° and 300°; (2) corresponding boiling points for water and mercury; and (3) the boiling points of naphthalene, benzophenone, and diphenylmethane, over a considerable range of pressure. H. M. D.

Heat Effect of Solution and Pressure of Saturated Vapour over Solutions. M. Levalt-Ezerski (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 787—805).—The author has developed further the considerations of his earlier papers (A., 1912, ii, 737; this vol., ii, 228) in conjunction with the conclusions drawn by Schiller (*Ann. Phys. Chem.*, 1894, [iii], **53**, 396; *ibid.*, 1897, [iii], **60**, 755. Compare A., 1899, ii, 357; 1906, ii, 220).

As regards the dependence of the pressure of a saturated vapour over a solution on the concentration of the latter, two cases present themselves, the lowering of the vapour pressure proceeding (1) more and (2) less rapidly than the increase of concentration. The relations deduced by the author show that in case (1), which

is the more common, dilution of the solution is accompanied by contraction. When, however, dilution of the solution results in expansion, the change of the vapour pressure with the concentration follows case (2). A number of examples are cited in illustration of these rules, and the bearing of the latter on the heat effect of solution is also considered. T. H. P.

Two Convenient Forms of Receiver for Fractional Distillations under Diminished Pressure. MARSTON TAYLOR BOGERT (*J. Ind. Eng. Chem.*, 1915, **7**, 785—786).—The apparatus consists of a vertical, graduated glass cylinder having a tubulure at the top, by which it is attached to the condenser; the cylinder has a tapped stem, which passes through a rubber stopper into a suitable vessel for receiving the distillate collected in the cylinder. A side-tube on the stem is fitted with a three-way tap, and is connected with a pump, a tube from the top of the cylinder, provided with a tap, being also connected with the tube leading to the pump. When the first fraction has been collected in the cylinder, it is discharged into the lower vessel, the tap on the stem and that on the tube leading from the top of the cylinder are closed, and the three-way tap turned so as to admit air to the lower vessel, which is then removed, and another attached in its place. The air may be exhausted from the latter by placing it in connexion with the pump through the three-way tap before the other taps are opened. In another form of the apparatus, a secondary pump is required to exhaust the air from the lower vessel. W. P. S.

Thermal Properties of Carbonic Acid at Low Temperatures. II. C. FREWEN JENKIN and D. R. PYE (*Phil. Trans.*, 1915, [*A*.], **215**, 353—381).—The experiments described in a previous paper (*ibid.*, 1914, [*A*], **213**, 67) have been continued in order to complete the entropy-temperature diagram, and to provide material for the construction of the total heat-entropy diagram. The data are mainly of interest in connexion with the use of carbon dioxide in refrigeration. Tables are given showing the specific heat of gaseous carbon dioxide at temperatures between −30° and 30°, and at pressures varying from 150 to 700 pounds per square inch. H. M. D.

Free Energy of Nitrogen Compounds. GILBERT N. LEWIS and ELLIOT Q. ADAMS (*J. Amer. Chem. Soc.*, 1915, **37**, 2308—2316).—The free energy of formation (F° 298) of some nitrogen compounds has been calculated from existing data, with the following results, expressed in calories: ammonia (gas), −4740; ammonia (liquid), −3490; ammonia (in aqueous solution), −7130; ammonium hydroxide (in aqueous solution), −63,750; the ammonium ion ($NH_4^{\cdot}$), −19,895; nitric oxide (gas), 20,850; nitrogen dioxide, NO_2 (gas), 13,250; nitrogen tetroxide, N_2O_4 (gas), 25,300; the nitric ion (NO_3'), −23,100; the nitrous ion (NO_2'), −7410; and nitrous acid (in aqueous solution), −11,980. E. G.

Free Energy of Formation of Formic Acid. GERALD E. K. BRANCH (*J. Amer. Chem. Soc.*, 1915, **37**, 2316—2326).—In connexion with a study of the free energy of organic compounds, Lewis and Burrows (A., 1913, ii, 23) have pointed out that it is desirable that the free energy of a few typical compounds should be known with reference to the elements of which they are composed. A study has now been made of the free energy of formation of formic acid.

The decomposition of formic acid into carbon monoxide and water has been found to be reversible, and to be catalysed by mineral acids. The equilibrium between carbon monoxide and water on the one hand, and formic acid dissolved in water acidified with hydrochloric acid on the other, has been measured at 218° and 156°. The partial pressure of formic acid from a similar solution has also been determined. From the data thus obtained, and the free energies of water and carbon monoxide (Lewis and Randall, A., 1914, ii, 802; 1915, ii, 227), the free energy of formic acid has been calculated. For the reaction $C(graphite) + H_2 + O_2 = H{\cdot}CO_2H$, the free energy of formation ($\Delta F°$ 298) has been found to be $-85{,}200$ cals. E. G.

The Heat Developed by a Solid Substance Passing into the State of Saturated or Dilute Solutions. Case of Sea Salt. ALB. COLSON (*Compt. rend.*, 1915, **161**, 414—416).—The author has determined the molecular heats of solution of sodium chloride at various stages of dilution by measuring the heat absorbed by solution of a known weight of the salt in a known volume of water. The difference between these values and those obtained for the heat absorbed by dilution of a saturated solution down to the given dilution gives the heat absorbed during the passage from the solid state into that of a saturated solution at any given temperature. The results show that the molecular heat of solution, for a saturated solution, is -460 cal. at 15°, and varies but little with rise or fall in temperature. For solutions containing 12·5 grams per litre, the molecular heat of solution is -1540 cal. at 7°, and this value diminishes to -1120 cal. at 22°, and to -1472 cal. at 7°, for a concentration of 36 grams per litre.

W. G.

Heat of Solution in Mixed Solvents. S. TANATAR (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1279—1286).—The author has previously shown (A., 1895, ii, 36) that, when dissolved in mixtures of alcohol and water, both non-electrolytes and electrolytes absorb more heat than when dissolved in water alone. From the results of measurements of the heats of solution of various electrolytes and non-electrolytes in mixtures of methyl or ethyl alcohol with water, Kolossovski (A., 1913, ii, 22, 308, 671, 672) concluded that alcohols form hydrates with development of heat, and that when a substance is dissolved in an aqueous alcohol it displaces the alcohol from its hydrate and forms a hydrate with the water. The author finds, however, that the excess of the heat absorbed on dissolving a sub-

stance in aqueous alcohol over that obtained when water alone is the solvent is often far greater than the heat of mixing of alcohol and water.

A systematic investigation of this question has been undertaken, carbamide being used as solute in order to eliminate the influence of variation in the degree of ionisation. Among non-electrolytes, carbamide is distinguished by its marked and rapid solubility in water and in methyl and ethyl alcohols of all concentrations up to 100%. The measurements were made at 15—18° in a Berthelot calorimeter, and in the calculation of the results the specific heats of the dilute solutions (5 grams in 300 c.c. of solvent) used were taken to be identical with those of the solvents (compare Kolossovski, *loc. cit.*). The results show that the negative heats of solution of carbamide in mixtures of alcohol with water are greater than in water or the alcohol alone, the maximal differences being for mixtures containing from 24—30% of the alcohol. The fact that the heat of solution is independent of the concentration of the carbamide is in disagreement with Kolossovski's theory.

Measurements were also made of the heats of solution of mercuric chloride, potassium iodide, succinic and picric acids, and *iso*propyl alcohol in water, and 24%, 30%, and 99—100% solutions of ethyl alcohol in water, and of mercuric chloride and picric and succinic acids in 24%, 30%, and 99—100% solutions of methyl alcohol in water. The results obtained with these compounds are not so accurate as those given by carbamide, owing to the greater times required for dissolution.

No cause can yet be assigned to the increased absorption of heat observed on dissolution in aqueous alcohols. It is, however, noteworthy that maximal viscosities of the aqueous alcohols very nearly correspond with the maximal absorptions of heat.

T. H. P.

The Pressure Balance and the Isothermals of Air, Argon, and Helium between 0° and 200°. L. Holborn and H. Schultze (*Ann. Physik.*, 1915, [iv], **47**, 1089—1111).—The pressure balance described in a previous paper (Holborn and Baumann, *ibid.*, 1910, [iv], **31**, 945) has been employed in the investigation of the pressure-volume relationships up to a pressure of 75 m. of mercury in the case of air and argon, and 40 m. for helium. The results obtained for air at 0° and 100°, when compared with the observations of Amagat, Witkowski, and Koch, show quite appreciable differences. The following table summarises the results obtained, in that the relative values of pv are recorded for a pressure of one metre of mercury and also for the highest pressure investigated. For each gas $pv=1$ at 0° and 1 m. pressure.

	Air.		Argon.		Helium.	
$t°$.	$p=1$.	$p=75$.	$p=1$.	$p=75$.	$p=1$.	$p=40$.
0°	1·0000	0·9712	1·0000	0·9270	1·0000	1·0271
50	1·1838	1·1918	1·1839	1·1535	1·1829	1·2091
100	1·3674	1·4003	1·3676	1·3646	1·3659	1·3915
150	1·5509	1·6013	1·5512	1·5681	—	—
200	1·7344	1·7977	1·7347	1·7658	—	—

The results obtained for argon are of particular interest, in that its behaviour shows considerable variation within the limits of temperature at which the *pv* relations were examined. At 0° and 50°, the value of *pv* for argon decreases continuously with increasing pressure; at 150° and 200° *pv* increases continuously with the pressure. At 100° *pv* decreases from 1·3671 at $p=1$ to a minimum value of 1·36205 at 45 m., and then increases up to 1·3646 at 75 m. of mercury. H. M. D.

Density and Viscosity of Aqueous Solutions, with Special Reference to Nitric Acid. Part I. Densities. WILLIAM ROBERT BOUSFIELD (T., 1915, **107**, 1405—1426).—The densities of *N*-, *N*/2-, *N*/4-, *N*/8-, *N*/16-, and *N*/32-nitric acid have been determined at 4°, 11°, 18°, and 25°. The measurements were made by means of a pyknometer previously described by the author (T., 1908, **93**, 679), and the results are given to six places of decimals and are accurate to ±5 in the sixth place. The experimental values are compared with values calculated by means of the contraction function χ, and it is shown that the two series agree to within +6 and −5 units in the sixth decimal place. The contraction function χ is defined by the expression $\chi=v(\rho/\rho_w-1)$, in which v is the volume of solution which contains E grams of dissolved substance and H grams of water, and $\rho=1/v=$density of solution and $\rho_w=1/w=$density of water. The properties of the contraction function are discussed, and its relationships to other well-known functions are demonstrated mathematically. Among the relationships considered are: (1) that with the U function, which correlates the vapour pressure and osmotic pressure, $U=v-P\,.\,dv/dP$ (Callender, A., 1908, ii, 671); (2) that with specific volume-percentage curves; (3) that with the eutectic point; and (4) that with the hydration function γ. The relationships are illustrated by reference to sulphuric acid solutions at 15°, nitric acid solutions at 14·2°, and sucrose solutions at 20°. J. F. S.

Physico-chemical Force of Attraction. II. L. G. GURVITSCH (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 805—827. Compare A., 1914, ii, 435).—The author's further investigations on this subject have been carried out with pure solvents, since with solutions the phenomena of adsorption are somewhat complicated, in consequence of the simultaneous adsorption of both solvent and solute.

With the three adsorbents, floridin, bone black, and alumina, calorimetric measurements have been made of the amounts of heat developed when 1 gram of the adsorbent is thoroughly moistened with each of a number of liquids. With floridin and alumina, the values thus obtained range from 57·1 and 78·8 cal., respectively, for amylene, to 3·9 and 7·2 cal., respectively, for hexane; with bone black, appreciably lower numbers are obtained in most cases. With all three adsorbents, the highest values are given by compounds containing either double linkings or oxygen or nitrogen, that is, by compounds which show the greatest tendency to purely chemical combination, whilst the lowest numbers are those for

saturated compounds, such as the paraffin hydrocarbons, carbon disulphide, and carbon tetrachloride. That there is no question of the formation of molecular compounds, which might support Werner's theory of supplementary valencies, is, however, shown by the absence of stoïcheiometrical relations between the proportions of different liquids adsorbed.

The results obtained with equal weights of floridin, infusorial earth, blood charcoal, and bone black show that, when exposed to the saturated vapours of different liquids, each of these adsorbents takes up the liquids in constant volumes. Thus, the particles of an adsorbent possess, at a certain temperature, a definite sphere of action independent of the nature of the adsorbed substance. Each particle of a particular adsorbent is surrounded by a spherical layer of molecules of the liquid, the thickness of this layer being the same for different liquids; since, however, the heats of adsorption vary, the molecules of different compounds must be held, in these layers, with greatly different forces.

The most probable cause of these results is the existence in the chemical molecule, even of a so-called saturated compound, of a residue of energy, intermediate in character to chemical and physical energy. Since the heats of absorption of different liquids by different adsorbents do not form perfectly parallel series, the heat of adsorption cannot be a measure of this "residual energy." Regularities do, however, occur among the heats of adsorption of allied compounds, and this is the case with either floridin or bone black or alumina, in spite of the marked chemical differences between these adsorbents. For instance, with the hydrocarbons, the heat of adsorption increases in the passage from the paraffins and naphthenes to aromatic compounds, and from the latter to ethylenic hydrocarbons. The ratio of the heats of adsorption of benzene and hexane has the values 1·19, 1·25, and 1·37, respectively, for the above adsorbents. In all three cases, chloroform develops 1·6—1·8 times as much heat as carbon tetrachloride; acetone always gives more heat than ethyl acetate, and methyl alcohol more than ethyl, and this more than amyl. In separate classes of similar compounds, the heat of adsorption may, therefore, serve as an approximate measure of the residual energy.

Parallelism exists in many cases between the residual energy, expressed by the heat of adsorption, and the ability to enter into purely chemical reaction. Thus, three similar series are formed by the heats of adsorption of methyl, ethyl, and amyl alcohols, the velocities with which these alcohols undergo esterification, and the heats of formation of their complex compounds with magnesium propyl iodide (compare Tschelincev, A., 1913, ii, 924). Further, almost complete parallelism exists between the heats of adsorption of a number of solvents and the magnitudes of the influence these exert on the velocity of formation of tetra-ethylammonium iodide from triethylamine and ethyl iodide; it would appear that the greater the residual energy of a solvent, that is, the stronger the attraction between its molecules and those of the reacting substances, or, in other words, the more the solvent is capable of con-

tiguity with these substances, the more readily will the reaction proceed.

When floridin is introduced into hexane, it falls to the bottom and leaves the supernatant liquid almost perfectly transparent, whilst in the case of acetone the latter becomes very turbid. Microscopic observation shows that, in the latter case, small particles become detached from the floridin grains. By collecting these separated particles on a weighed filter, a quantitative, although only approximate, measure of the percentage disintegration of the floridin is obtained. The numbers thus found exhibit complete parallelism to the heats of adsorption, and the phenomenon represents a direct transformation of chemical into mechanical energy. Parallelism with the heats of adsorption of solvents by floridin is also shown by the solubility in these solvents of benzoic acid, nitrobenzene, and trimethylamine.

That the same force forms the basis of the phenomena of adsorption and those of solubility is shown also by the parallelism between the heats of adsorption and the constants of internal contraction calculated by Tammann, who found ("Innere Kräfte der Losungen," 89) that the contraction constant ΔK is greater for water than for alcohol or acetone, and greater still than for ether and carbon disulphide.

A similar connexion is observable on comparison of the author's numbers with (1) the results of Biron's measurements of the change of volume occurring when liquids are mixed (A., 1910, ii, 394), this change becoming less as the residual energies of the two liquids approach one another the more closely; (2) the latent heats of evaporation of liquids at their boiling points; (3) the dielectric capacities of the liquids; (4) the internal pressure of liquids (compare Walden, A., 1909, ii, 547); (5) the surface tensions of liquids of similar chemical character.

These results furnish a foundation for the conclusion that one and the same residual chemical energy forms the basis of all those diverse physico-chemical phenomena and processes which depend on the mutual attraction of similar or dissimilar molecules. No molecular process can, therefore, be regarded as of a purely physical character, the residual chemism manifesting itself in every reciprocal molecular action. The chemical action between two substances, A and B, may be expressed by the general formula $P=f(a, b, C)$, where a and b are the constants of chemical energy or the chemical potentials of A and B respectively, each being independent of the nature of the other substance, and C is a magnitude which, although not a function of a and b, is specific for the given pair, A and B. A general function of similar type, but including the distance, ρ, between the reacting molecules, may be assumed for molecular physico-chemical processes, $\pi=\phi(\alpha, \beta, \Gamma, \rho)$, α and β representing the residual chemical potentials.

Besides, by the absence of stoïcheiometric relations, the physico-chemical force of attraction differs from purely chemical forces in two properties: (1) The action of the force of chemical affinity, resulting in the formation of chemical compounds with more or

less simple stoïcheiometric relations, is limited in its action to atomic distance, or, at most, to the distances separating neighbouring molecules. The sphere of action of the physicochemical forces of attraction is many times greater than this. Experiments on adsorption by silver foil and glass wool immersed in the saturated vapours of carbon tetrachloride, carbon disulphide, and acetone gave, for the thickness of the layer of adsorbed liquid, 35, 33, and 28.10^{-6} mm. with the former adsorbent, and 30, 31, and 26.10^{-6} mm. with the latter; these layers are several tens of molecules in thickness. (2) In general, the intensity of the action between any two elements increases with the diversity in nature of the elements, whereas with the action of residual chemical energy the reverse holds good.

The experimental part of the paper contains a brief account of (1) the compounds used; the floridin contained: H_2O, 17·88; CO_2, 0·20; SiO_2, 55·28; Al_2O_3(mainly) + Fe_2O_3, 21·05; $CaO + MgO$, 4·29; and $K_2O + Na_2O$, 1·89%; (2) the apparatus and methods used in the calorimetric measurements; and (3) the method of studying the adsorption from vapours. T. H. P.

[**Physico-chemical Force of Attraction.**] L. G. Gurvitsch (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1310—1312).—Reply to Kolosovski's criticisms (this vol., ii, 532) of the author's work (A., 1914, ii, 435). T. H. P.

The Temperature-coefficients of the Free Molecular Surface Energy of Liquids between −80° and 1650°. X. Measurements Relating to a Series of Aliphatic Compounds. F. M. Jaeger and Jul. Kahn (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 269—285. Compare this vol., ii, 613).—Further measurements have been made of the surface tension and of its variation with temperature. The results are given in the following summary, which shows the temperature-coefficients of the molecular surface energy and the equations for the change of density with the temperature. Where the temperature-coefficient changes with the temperature, the limiting values are given, the first value relating to the lowest range of temperature: ethyl iodide, 1·43—1·84; ethylene chloride, 2·16, $D = 1·2826 - 0·001446t$; ethylidene chloride, 2·00—1·43, $D = 1·2069 - 0·0016t + 0·^{6}15t^2$; acetylene tetrachloride, b. p. 146·3°/758 mm., 2·36, $D = 1·6197 - 0·001738t + 0·^{5}264t^2$; acetylene tetrabromide, b. p. 132°/20 mm., 2·51, $D = 2·9956 - 0·00204t - 0·^{6}64t^2$; epichlorohydrin, b. p. 117°/758 mm., 2·04—1·41, $D = 1·2406 - 0·00114t - 0·^{5}16t^2$; carbon disulphide, m. p. −111·6°, 1·75, $D = 1·2921 - 0·00147t$; methyl alcohol, 0·67, $D = 0·8102 - 0·000905t - 0·^{7}85t^2$; formic acid, 0·57—1·15, $D = 1·2441 - 0·001249t - 0·^{6}181t^2$; monochloroacetic acid, 0·96—1·84, $D = 1·3878 - 0·001182(t-50) - 0·^{5}104(t-50)^2$; dichloroacetic acid, 2·30, $D = 1·5924 - 0·001378t$; trichloroacetic acid, 1·09—1·82, $D = 1·6216 - 0·001566(t-50) - 0·^{6}72(t-50)^2$; lævulic acid, 1·33, $D = 1·1557 - 0·000814t - 0·^{6}4t^2$; nitromethane, 1·14—1·58, $D = 1·1657 - 0·0015052t + 0·^{5}2629t^2$; bromonitromethane, b. p. 152·5°/

765 mm., m.p. −28°; hexonitrile, b.p. 157°/762 mm., m.p. −45°, 1·63—1·84, $D=0·8347-0·000806t-0·0^{5}12t^{2}$; methyl succinate, b.p. 103·5°/25 mm., 2·32, $D=1·1441-0·001184t+0·0^{6}64t^{2}$; ethyl bromo*iso*succinate, b.p. 122°/13 mm., 2·54, $D=1·3499-0·00128t+0·0^{6}64t^{2}$; acetylacetone, m.p. −30°, b.p. 137·5°/75 mm., 2·17—1·60—2·06, $D=0·9979-0·0^{4}56t+0·0^{6}96t^{2}$. The fall and subsequent rise in the temperature-coefficient for acetylacetone is probably connected with the displacement of the keto-enol equilibrium.

The results obtained in this investigation show that, in general, the temperature-coefficients of related compounds change with the temperature in a similar manner. H. M. D.

Temperature-coefficients of the Free Molecular Surface Energy of Liquids Between −80° and 1650°. XI. The Surface Tension of Homologous Triglycerides of the Fatty Acids. F. M. Jaeger and Jul. Kahn (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 285—296. Compare preceding abstract).—The data are summarised as in the preceding abstract: glycerol, 6·1—1·5, $D=1·2720-0·000576t-0·0^{6}64t^{2}$; glyceryl triformate, 2·20, $D=1·3319-0·001014t$; glyceryl triacetate, 0·64—3·0, $D=1·1874-0·00129t+0·0^{5}17t^{2}$; glyceryl tributyrate, 1·70—2·63, $D=1·0596-0·00101t+0·0^{6}8t^{2}$; glyceryl trihexoate, 2·49, $D=1·0113-0·000852t+0·0^{6}48t^{2}$; glyceryl trioctoate, 2·12—2·90, $D=0·9673-0·000824t+0·0^{6}48t^{2}$; glyceryl tridecoate, 3·09, $D=0·9475-0·000698t$; glyceryl trilaurate, 3·33, $D=0·9005-0·00060(t-50)-0·0^{6}24(t-50)^{2}$; glyceryl tripalmitate, 5·55—3·41, $D=0·8851-0·000578(t-50)-0·0^{6}79(t-50)^{2}$; glyceryl stearate, 6·75, $D=0·8859-0·000606(t-50)-0·0^{6}56(t-50)^{2}$; glyceryl trioleate, 8·4—3·25, $D=0·9371-0·00081t+0·0^{5}104t^{2}$.

The surface tension of butter and margarine was also measured. The temperature-coefficient for margarine is greater than that for butter. The surface tension-temperature curves cross at about 50°. H. M. D.

Temperature-coefficients of the Free Molecular Surface Energy of Liquids between −80° and 1650°. XII. The Surface Energy of the Isotropic and Anisotropic Liquid Phases of some Aromatic Azoxy-compounds and of Anisaldazine. F. M. Jaeger and Jul. Kahn (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 297—304. Compare preceding abstracts).—A number of substances which form anisotropic liquids have been examined in order to ascertain the effect of the transition from the anisotropic to the isotropic condition on the temperature-coefficient of the molecular surface energy. The results obtained for *p*-azoxyanisole, *p*-azoxyphenetole, and *p*-anisaldazine show that the surface energy decreases more quickly with rise of temperature in the anisotropic form than in the isotropic modification. The surface energy increases at the transition temperature, but this change is gradual, and is observable at temperatures below that at which the anisotropic liquid is converted into the isotropic form.

Ethyl *p*-azoxybenzoate and ethyl *p*-ethoxybenzylideneamino-*α*-methylcinnamate have also been examined. The former melts at 114°, and the anisotropic liquid clears at 121°. The molecular surface energy of the anisotropic form decreases with rise of temperature, whilst that of the isotropic modification first decreases and then increases. The latter substance has m. p. 169°, and the anisotropic liquid becomes isotropic at 186°. The surface energy decreases with rise of temperature in the case of the crystalline liquid, whilst that of the isotropic form first decreases, then increases, and later diminishes as the temperature rises.

H. M. D.

The Drop-weight method for Determining Surface Tensions. Allan Ferguson (*Phil. Mag.*, 1915, [vi], **30**, 632—637).—A discussion of the drop-weight method as applied by Morgan (compare A., 1914, ii, 32, 33) in the determination of the surface tension of liquids. Although there is no a priori reason for the assumption that the results obtained by this method are influenced by the contact-angle, it has been found that for seventy out of a hundred liquids which have been subjected to measurement, the values of the surface tension are in good agreement with those obtained from observations on the capillary rise. The author considers that the differences met with in the remaining thirty liquids are probably due to the existence of a finite angle of contact at the liquid-glass interface. For ethyl ether at 20°, the angle of contact is about 16°, and in this case Morgan's value (16·13 dynes per cm.) differs, not only from the value (16·49) given by the method of capillary rise, but also from that (17·30) afforded by Jaeger's method, which is independent of the contact angle. Much of the available experimental material cannot be interpreted in any exact manner until the question of the contact-angle has been solved.

H. M. D.

The Viscosity of Colloidal Solutions. E. H. Büchner (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 170—173).—The relation between the viscosity, η', of a suspension and that of the dispersive medium, η, can be represented, according to Einstein, by the equation $\eta'-\eta/\eta=2{\cdot}5v'/v$, in which v' is the volume of the suspended particles in volume v of the suspension. This formula may be applied in calculating the volume occupied by the disperse phase in colloidal solutions.

From observations made with colloidal solutions of molybdenum-blue (Mo_3O_8 ?) and ferric hydroxide, it is found that the density of the suspended particles is much smaller than that of the substances in the free condition. This is interpreted in favour of the view that the colloidal particles contain water. The proportion of water which thus becomes associated with the colloid is greater for ferric hydroxide than for molybdenum-blue. H. M. D.

Kinetics of Adsorption. Oskar Arendt (*Koll. Chem. Beihefte*, 1915, **7**, 212—250).—A complicated apparatus is described by means of which the author has been able to make measurements of

the velocity of adsorption in cases where the process takes place very rapidly, and is practically complete at the end of a few seconds. Most of the observations were made with solutions of soluble starch and strontium carbonate as the adsorbent.

In agreement with previous observations, the results show that the velocity of adsorption increases very considerably with the rate of stirring. The quantity of starch adsorbed after a given time interval, relative to that which is finally adsorbed, is found to be independent of the concentration of the starch solution. The temperature-coefficient of the adsorption velocity is about 1·1, which is less than the coefficient which expresses the influence of temperature on pure diffusion processes. The equilibrium condition is more rapidly attained at higher temperatures. H. M. D.

Osmotic Pressure. J. J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 184—190).—A criticism of the views put forward by Ehrenfest (this vol., ii, 425), in which the author lays down the conditions which must be satisfied in any attempt to interpret the phenomenon of osmotic pressure on a kinetic basis. H. M. D.

Molecular Allotropy and Phase Allotropy in Organic Chemistry. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 346—362).—A theoretical paper in which the author discusses the equilibrium relations in a pseudo-ternary system consisting of two mutually convertible isomerides in contact with a solvent. According to van't Hoff, the ratio of the concentrations of the two isomerides in any solution in which equilibrium has been attained is determined by the relative solubilities of the isomerides in the solvent, as expressed by the equation $C_A/C_B = GL_A/L_B$, in which C^A and C_B are the equilibrium concentrations, L_A and L_B the solubilities of A and B in the pure solvent, and G is a constant which is independent of the nature of the solvent. As pointed out by Dimroth (A., 1911, ii, 31), the validity of this relation permits of the calculation of the state of equilibrium in any solvent if the solubilities of the two isomerides in this solvent are determined.

It is shown that the above equation represents merely an ideal limiting case, and that it is not applicable when the saturated solutions are so concentrated that the solubilities of the two isomerides are mutually affected. The equation requires modification in the sense that L_A/L_B represents the ratio of the concentrations of the two isomerides in the solution which is saturated simultaneously with respect to both forms. H. M. D.

The Apparent Contradiction between Theory and Practice in the Crystallisation of Allotropic Substances from Different Solvents. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 363—369. Compare preceding abstract).—The equation connecting the equilibrium between mutually convertible isomerides in a solution and the solubility ratio as modified in the manner

indicated in the preceding paper, is deduced by thermodynamic reasoning.

The experimental evidence, which was considered by Dimroth to contradict the relation deduced by van't Hoff, is not necessarily in disagreement with the modified equation. H. M. D.

Supersaturation and Release of Supersaturation. DEVENDRA NATH BHATTACHARYYA and NILRATAN DHAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 369—373).—Experiments have been made to ascertain the facility with which different substances form supersaturated solutions. The results obtained admit of no general conclusion, but it is apparent that supersaturated solutions are readily formed by substances which yield crystalline hydrates, and that the phenomenon is frequently shown by readily soluble substances and by substances which form large, well-defined crystals. H. M. D.

The Density and Refraction of Colloidal Solutions. ROBERT WINTGEN (*Koll. Chem. Beihefte*, 1915, **7**, 251—282).—Measurements have been made of the density and refractive index of colloidal solutions of arsenic trisulphide, antimony trisulphide, silicic acid, molybdic acid, ferric hydroxide, and tannin. The results show that the density and refractive index of the solutions are linear functions of the concentration (grams of the dispersive phase per 100 c.c. of solution), whilst the specific volume and the product of the specific volume into the refractive index are linear functions of the percentage content of the disperse phase. These relations have been deduced on the assumption that the density and refractive index of the disperse phase and the dispersive medium are independent of their relative proportions in the mixtures.

In all cases the density of the disperse phase was found to be greater than that of the same substance in the amorphous form.

H. M. D.

Negative Hydroxide Sols. H. FREUNDLICH and WALTHER LEONHARDT (*Koll. Chem. Beihefte*, 1915, **7**, 172—211).—The properties of colloidal solutions of molybdenum dioxide (MoO_2,H_2O) and of vanadium pentoxide have been examined in detail in the expectation that these negatively charged hydroxides might afford further information relative to the connexion between the phenomena of precipitation and adsorption.

Colloidal solutions of molybdenum dioxide cannot, in general, be completely coagulated by the addition of electrolytes. According to experiments in which it was subjected to dialysis, the residual coloured solution appears to be colloidal. Comparative measurements of the quantities of electrolytes which suffice to cause turbidity show that the coagulation is merely due to the cation. The coagulating capacity increases with the valency of the cation, but the univalent ions differ very considerably amongst themselves. In the series of alkali metal ions, the concentration which produces turbidity decreases in the ratio of about 100:1 in passing from lithium to cæsium. Organic cations and cations of the heavy

metals are frequently more active than would be anticipated from the valency. The coagulated dioxide shows differences in the readiness with which it undergoes peptonisation, in that the sol form is more readily produced from coagulates which have been precipitated by the less active electrolytes. Low temperature is also favourable to the re-formation of the sol.

Colloidal solutions of vanadium pentoxide exhibit striking optical properties. When stirred, they present the appearance which would be observed by a liquid in which a mass of fine crystals is suspended. If examined between crossed Nicols, the slightest disturbance of the solution causes illumination of the dark field. The behaviour of the solutions towards electrolytes is very similar to that found with solutions of molybdenum dioxide, and similar variations are found in regard to the peptonisation of the coagulate which has been thrown down by the action of different electrolytes.

The positive colloids, ferric and aluminium hydroxide, are coagulated by the negatively charged vanadium pentoxide. The quantity of this which is necessary for the coagulation of a given quantity of the positive colloids referred to is very small in comparison with the quantities of arsenic trisulphide, antimony trisulphide, and other negative colloids. It would seem, therefore, that the colloidal particles of vanadium pentoxide carry a relatively much larger electric charge. H. M. D.

Sol- and Gel-Condition of Gelatin Solutions. I. Gelatinisation. II. Swelling. L. Arisz (*Koll. Chem. Beihefte*, 1915, **7**, 1—90).—The experiments described in this paper were made with the object of tracing the changes which take place in solutions of gelatin when these are subjected to variations of temperature or to changes in concentration at constant temperature. The measurement of the viscosity was made use of in detecting and following the changes in the condition of the gelatin. The results obtained show that the solutions only reach a state of equilibrium after the lapse of a considerable interval of time, and this applies to the changes which are brought about by variations of temperature and concentration. Similar slow changes are found to take place in the gel condition.

Observations on the swelling of gelatin under different conditions lead to the view that the swelling is accompanied by an increase in the size of the gelatin particles and by a reduction in the intensity of the forces which hold these particles together. The effect of temperature and of the age of the gels on the swelling capacity can be explained in terms of this hypothesis without assuming that the gels are possessed of a honey-comb structure.

H. M. D.

The Spontaneous Formation of Metallic Colloids in Contact with a Dispersive Medium. H. Nordensen (*Koll. Chem. Beihefte*, 1915, **7**, 91—109).—According to Traube-Mengarini and Scala (A., 1911, ii, 116; 1912, ii, 161), colloidal solutions of many metals are

obtained when these are brought into contact with dispersive media, such as water and ethyl alcohol. Further experiments by the author have failed to confirm the above observation, and his results lead to the conclusion that in no case are metallic colloids formed by the spontaneous dissolution of the metals. When oxidisable metals are submitted to the action of water, colloidal solutions of the oxide or hydroxide are sometimes obtained, but the effect in such cases is primarily due to chemical action between the metal and traces of oxygen. Colloidal solutions of this nature are formed by lead in contact with water and many organic solvents. Silver is also very readily attacked by oxygen both in water and in ethyl alcohol, and the resulting colloidal oxide is subsequently transformed into metal, so that in this case colloidal metal solutions are obtained. The formation of the colloidal silver is, however, a secondary effect, and cannot be interpreted as evidence of the spontaneous disintegration of the solid metal.

H. M. D.

The Formation of Colloidal Metals by the Action of Light, Röntgen, and Radium Rays on Metals in Contact with a Dispersive Medium. H. Nordensen (*Koll. Chem. Beihefte*, 1915, **7**, 110—136. Compare preceding abstract).—Previous experiments on the action of ultra-violet light and Röntgen rays on metals in contact with water and other dispersive media (Svedberg, A., 1909, ii, 23, 277) have been interpreted as affording evidence that colloidal solutions of the metals are formed in these circumstances. The further investigation of this question has shown that light, Röntgen, and radium rays have no effect beyond that of accelerating the changes which take place in the absence of these rays. Gold and platinum are entirely unacted on. The oxidisable metals yield colloidal solutions of the oxides or hydroxides. In the case of silver, the initially formed colloidal oxide is rapidly reduced under the influence of ultra-violet rays, and colloidal silver is thereby obtained. H. M. D.

Chemical Equilibrium and Action of Neutral Salts. G. Poma and G. Albonico (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 43—50. Compare this vol., ii, 620).—The influence of the presence of certain chlorides and other salts on the esterification of acetic and other acids by methyl and other alcohols has been investigated. The conclusions drawn from the results obtained and from those previously described are as follows.

The presence of a neutral salt displaces the homogeneous equilibrium of esterification and hydrolysis, part of the water present being apparently withdrawn from the reaction. Such displacement depends on the concentration of the neutral salt and on the nature of its cation, increasing rapidly with diminution of the electro-affinity of the cation; the series K, Na, Li, Ca, Mg represents the order of increasing activity of salts of one and the same acid. A less marked, but appreciable, action is exerted by the nature of the anion; thus, 2 mols. of lithium chloride, bromide,

or nitrate per litre diminish the equilibrium constant by 35·7%, 40%, or 37·5%. The view that neutral salts in solution form hydrates which increase in complexity as the electro-affinity of the ions of the salts diminishes, is not in agreement with the equality of the diminutions of the equilibrium constant produced by equal amounts of lithium chloride when added to systems with values of from 2 to 10 for the initial molecular relation between the water and ethyl alcohol. The observations are, however, in accord with the hypothesis advanced to explain the action of neutral salts on the apparent concentrations of cupric ions (compare Poma and Patroni, A., 1914, ii, 440; Poma, this vol., ii, 210).

As a rule, the accelerating action exerted by neutral salts on the separate velocities of esterification and hydrolysis increases with the affinities of the salts for water; this result differs sharply from that obtained by studying the action of neutral salts under ordinary conditions (compare A., 1911, ii, 707). T. H. P.

Photochemical Temperature-coefficient of Chlorine. A. V. Nazarov (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 943—955).—Photochemical effects are now usually regarded, at least as far as their initial stages are concerned, as photoelectric effects, and since the latter are independent of the temperature, and since, further, the velocity of a photochemical reaction depends on the mass of the activated molecules, and this on the velocity of activation, it follows that the temperature-coefficients of photochemical processes should be less than those of reactions occurring in the dark. The experimental numbers vary, indeed, from 1·02 to 1·40 (compare Plotnikov, A., 1912, ii, 218). It appears probable that the temperature-coefficient of a photochemical reaction is a magnitude characteristic of the structure of the photochemical component which absorbs the light. Thus, in the absorption of light by molecules containing, as photochemical component, iodine or bromine, the temperature-coefficients have one and the same value, 1·40, and Plotnikov supposes that the same would be the case with chlorine. Support is lent to this view by Benrath and Tuchel's results (A., 1914, ii, 447), which give the value 1·395 for the temperature-coefficient of the conversion of an aqueous solution of chlorine into hydrogen chloride and oxygen.

The author has measured the velocity of the action of chlorine on cinnamic acid in carbon tetrachloride solution, both in the dark and in the light, at 18° and 8°, 31° and 21°, and 29° and 19°. Luther and Goldberg (A., 1906, ii, 641) drew the conclusion that, in presence of traces of oxygen, all photochemical reactions in which light forms the light-absorbing component exhibit induction periods. In the reaction studied by the author, such induction periods make their appearance, and, since small proportions of oxygen could not be eliminated from the reaction mixtures, these proportions were kept as nearly as possible the same in all cases in order that the induction periods might be virtually identical. A Uviol lamp carrying a constant current was employed as source of light, this being at a constant distance from the tube containing

the reacting mixture. In order to avoid loss of chlorine from the more concentrated solutions at the higher temperatures used, a pipette was connected by a three-way cock to the reaction tube and the flask in which the liquid was titrated with thiosulphate.

The calculation of the results was based on the assumption that the process occurring in the light is the sum of that taking place in the dark and the photochemical reaction, and, since the reaction proceeds practically linearly subsequent to the induction period, the velocity constants were calculated by the formula

$$K=(c_2-c_1)/(t_2-t_1),$$

where c_1 and c_2 are the concentrations of chlorine reacting in the light, and t_1 and t_2 the corresponding times. The values of the temperature-coefficients obtained are: $K_{18}/K_8=1{\cdot}406$, $K_{31}/K_{21}=1{\cdot}400$, and $K_{29}/K_{19}=1{\cdot}400$, the mean of the three being 1·402.

The high value, 1·5, obtained by Slator (T., 1903, **83**, 729) for the temperature-coefficient of the combination of chlorine with benzene in the light is explained by the fact that no allowance was made for the velocity of the reaction in the dark.

T. H. P.

Catalysis. XX. Reactions of Both the Ions and the Molecules of Acids, Bases, and Salts. Reaction of Sodium Ethoxide with Ethyl Bromide and Ethyl Iodide in Absolute Ethyl Alcohol at 25°. E. K. Marshall, jun., and S. F. Acree (*J. Physical Chem.*, 1915, **19**, 589—608. Compare A., 1913, ii, 576, 577, 688, 748; T., 1914, **105**, 2582; and this vol., ii, 406).—It is shown in the present paper that the theory that ions are the only chemically active portions of the electrolytes is only partly correct, and that much of the earlier work on which this theory was based had been incorrectly interpreted. The theory is therefore put forward that both the ions and the non-ionised parts of acids, bases, and salts, may undergo transformation with comparable velocities. A series of tables is given of the velocities of the reactions between sodium ethoxide with ethyl bromide and ethyl iodide in absolute ethyl-alcoholic solution at 25° at concentrations N, $N/2$, $N/4$, $N/8$, and $N/16$. The experimental data have been substituted in the general equation $K_N=K_i\alpha+K_m(1-\alpha)$, in which K_N is the observed velocity constant, K_i the velocity constant due to the ions, and K_m that due to the non-ionised molecule. From a series of simultaneous equations thus obtained, K_i and K_m have been calculated, and are shown to be real constants. This is interpreted as showing that both the ions and the non-dissociated salt react with the non-ionised alkyl haloid. In support of the theory, it is shown that the value of K_i, the velocity constant for ethoxide ions in reaction with a given alkyl haloid, is the same whether the ion is derived from sodium, potassium, or lithium ethoxide. J. F. S.

Reaction between Amylene and Trichloroacetic Acid in Different Solvents. G. E. Timofeev and L. M. Andreasov (*J. Russ Phys. Chem. Soc.*, 1915, **47**, 838—848).—The reaction between amylene and trichloroacetic acid, which in the simplest case should

proceed according to the equation $CCl_3{\cdot}CO_2H + C_5H_{10} \rightleftarrows CCl_3{\cdot}CO_2{\cdot}C_5H_{11}$ (1), has been investigated by Nernst and Hohmann (A., 1893, i, 449), who found that the action of the acid is proportional to the square of its concentration, and by Konovalov (A., 1907, ii, 854), who confirmed this result, and showed that the presence of hydrocarbon solvents exerted only a slight and uniform influence on the reaction, whilst that of ether lowered the limit of esterification considerably. The latter author drew the conclusion that an acid ester is formed,

$$C_5H_{10} + 2CCl_3{\cdot}CO_2H \rightleftarrows CCl_3{\cdot}CO_2{\cdot}C_5H_{11},CCl_3{\cdot}CO_2H \quad (2),$$

rise of temperature has a decomposing effect on this product.

Whether the reaction proceeds according to equation (1) or (2), a change occurs in the number of molecules, so that the esterification should depend on the volume; thus, either $C_1C_2/CV = K_1$ or $C_1C_2/CV^2 = K_2$. Addition to this system of a solvent may have a twofold effect: (1) Such addition is accompanied by increase of the volume, and so displaces the equilibrium from right to left, that is, lowers the esterification limit. In this respect, the action of all solvents should be uniform, and Konovalov (*loc. cit.*) with small additions, and the present authors with considerable additions, of solvents find this to be confirmed experimentally. (2) The solvent may, however, also exert an "active" influence, that is, may act chemically, on one of the reacting compounds, for instance, the trichloroacetic acid, forming with it a more or less stable compound, in accordance with the scheme $A + S \rightleftarrows S'$ (3), where A, S, and S' represent the acid, solvent, and solvate respectively. Consequently, the behaviour of different solvents should vary in dependence on their chemical nature, and this is found to be the case.

Pronouncedly basic solvents, such as aniline, by combining with the acid, should and do retard the esterification. Also, ether (Nernst and Hohmann, *loc. cit.*) exhibits considerable activity in retarding the esterification, owing to its ability to form oxonium compounds, and similar effects are produced by the other oxygenated solvents investigated, namely, acetone (compare Kobozev, A., 1904, i, 223), methyl ethyl ketone, and nitrobenzene.

As well as with a number of separate solvents, the authors have determined the limits of esterification at 25° and 50° with mixtures in various proportions of the following pairs of solvents; benzene + acetone, benzene + methyl ethyl ketone, benzene + nitrobenzene, and chloroform + acetone, the former member of each pair being "inactive" and the latter "active."

With benzene and acetone, small proportions of the latter cause marked lowering in the esterification limit at 25°, but when the proportion of acetone in the mixed solvent reaches 25—30%, further increase has little influence; the curve for 50° is of the same general character. Rise of temperature lowers the limit of esterification, and the curve for 50° at first lies below that for 25°, but subsequently crosses it, so that with large proportions of acetone the higher limit of esterification corresponds with the higher temperature. This phenomenon is regarded by the authors

as the result of the unequal rates at which the ester and the solvate decompose with rise of temperature, and is observed also with acetone and methyl ethyl ketone and with acetone and chloroform. With the latter mixture, the depressing effect of the acetone on the esterification limit is partly paralysed by the presence of the chloroform, which, according to Tsakalotos (A., 1908, ii, 260) and others, possesses feebly acid properties and forms a compound, probably $CMe_2{:}OH{\cdot}CCl_3$, with acetone.

In the case of benzene + nitrobenzene, small proportions of the latter cause, both at 25° and at 50°, an increase of 6% in the value of the esterification limit, which then falls as the proportion of nitrobenzene is increased further; no explanation of the appearance of this maximum is suggested. T. H. P.

Hydrolysis of Esters, Particularly the Ethyl Phthalates, by Alkalis. Rud. Wegscheider and Walter von Amann (*Monatsh.*, 1915, **36**, 549—610).—After a review of the literature dealing with ester hydrolysis by alkalis in aqueous or alcoholic solution, it is proved by mathematical reasoning that in kinetic investigations in aqueous–alcoholic solutions the equilibrium between sodium hydroxide and sodium ethoxide can be disregarded, and that the mixture of these two compounds can be treated as a single substance with a definite dissociation constant, provided that the ratio of the concentrations of water and alcohol is approximately constant.

The hydrolysis of ethyl hydrogen phthalate by a solution of sodium in 96·4% alcohol under certain conditions as to concentration at first sight appears to be a termolecular reaction, but that this result is apparent and not real is indicated by the facts that the "termolecular" constants obtained vary with the initial concentration, and also that if the solution of alkali metal is under 0·2*N*, the reaction is bimolecular between the undissociated portions of the sodium ethyl phthalate and the sodium ethoxide–hydroxide mixture. The remarkable result that the undissociated compounds are active in the hydrolysis under these conditions is to some extent analogous to other results of recent investigations with alcoholic hydrogen chloride.

The hydrolysis of normal ethyl phthalate by aqueous–alcoholic sodium hydroxide occurs in stages, and it is probable, again, that the undissociated portion of the sodium ethoxide–hydroxide mixture is active. The ratio of the velocity constants obtained for the first and second stages deviated appreciably from the value 2, although it was not widely different from this figure.

A mathematical discussion is given of the effect of the products of the reaction on the degree of dissociation of the participants. D. F. T.

Kinetics of the Reactions Occurring with Phthalic Acid and its Esters in Aqueous–Alcoholic Hydrogen Chloride Solution. Rud. Wegscheider and Walter von Amann (*Monatsh.*, 1915, **36**, 633—717).—The earlier portion of the paper gives a review of the

literature dealing with the esterification of alcohols in the presence or otherwise of a mineral acid as accelerator, and also with the hydrolysis of esters with aqueous or alcoholic hydrogen chloride solution.

Investigations of the action of alcoholic hydrogen chloride solution on phthalic acid and its esters are complicated by the interaction of the alcohol with hydrogen chloride. It is shown that the velocity of formation of ethyl chloride from hydrogen chloride and 96·4% alcohol in cases where the hydrogen chloride is of fair concentration is approximately proportional to the square of this concentration, thus indicating a catalytic effect. The reverse action, namely, between ethyl chloride and aqueous alcohol, appears to experience no catalysis.

In the reaction between phthalic acid and its ethyl esters with 96·4% alcohol containing hydrogen chloride in solution, the variation observed in the hydrogen chloride content can be referred entirely to the interaction of this acid and the alcohol, no appreciable saponification of ester with formation of ethyl chloride occurring. The only appreciable hydrolytic effect is that exerted by water on the normal ester, the acid ester being almost entirely unaffected. The esterification of phthalic acid occurs in two stages, the constants for the formation of the acid ester being much greater than those for the conversion of the acid ester into the normal ester, although at the same time they are less than the constants for the esterification of benzoic acid. When the esterification of phthalic acid in 96·4% alcohol containing hydrogen chloride has proceeded so far that the acid has been entirely converted into the acid ester, one-third of the latter has already undergone further conversion into the normal ester. The further esterification of the acid ester then proceeds until an equilibrium is reached, caused by the inverse hydrolysis of the normal ester by water, but this equilibrium is not permanent, because the quantity of water is slowly augmented by the interaction of the alcohol and hydrogen chloride; a gradual hydrolysis therefore ensues, until at last equilibrium is attained in both reactions.

In the course of the investigation, the density of alcoholic solutions of hydrogen chloride was determined at several concentrations and temperatures.

Mathematical treatment is given to the kinetics of a unimolecular reaction with a partly dissociated substance of which only the undissociated portion is active, the possibility of a concurrent inverse molecular reaction being also considered. The case of two consecutive reactions with unimolecular inverse reactions is also discussed, and still more complicated cases may be treated in a similar manner by separately considering small intervals during which the less variable quantities can be considered constant.

D. F. T.

Rate of Conversion of Cinchonine into Cinchotoxine. H. C. Biddle and O. L. Brauer (*J. Amer. Chem. Soc.*, 1915, **37**, 2065—2082).—Biddle and Rosenstein (A., 1913, ii, 492) have deter-

mined the rate of conversion of cinchonine into cinchotoxine in acetic acid of two different concentrations. The reaction has now been studied at 99·7° in presence of acetic acid through a wide range of concentrations, in presence of formic, propionic, oxalic, and hydrochloric acids of various concentrations, and in mixtures of acetic acid and hydrochloric acid. The polarimetric method of analysis was used almost exclusively.

The results show that the rate of conversion in presence of an organic acid gradually increases with the concentration of the acid, and, in the case of acetic acid, this is true between concentrations of 0·05 and 8·0 molal. Within this range, the velocity of the reaction seems to be some direct function of the concentration of the non-ionised acid. In glacial acetic acid (17·24 molal), the rate decreases and falls considerably below that at which the conversion proceeds in acid of 8·0 molal concentration. As has been shown previously (A., 1912, i, 296), the speed of conversion in presence of different organic acids of equal concentration decreases as the dissociation constant of the acid increases. The organic acid acts as a true catalytic agent, accelerating, but not causing, the reaction. The rate of conversion is decreased by the presence of the hydrogen ion, the introduction of hydrochloric acid gradually diminishing the velocity until at a certain concentration the reaction practically ceases. In solutions of different cinchonine salts, the rate of reaction increases with increasing concentration of the organic acid, but the rates for equal concentration are less in the case of salts, which by partial hydrolysis in solution give a greater concentration of hydrogen ions. E. G.

Rate of Conversion of Cinchonidine into Cinchotoxine. H. C. Biddle and R. H. Butzbach (*J. Amer. Chem. Soc.*, 1915, **37**, 2082—2087).—An account is given of experiments which show that the rate of conversion of cinchonidine into cinchotoxine at 99·7° is affected by the presence of organic acids in the same way as that of cinchonine (preceding abstract). The velocity of the reaction in presence of acetic or formic acid increases with increasing concentration of the acid. Increasing concentration of hydrogen ions causes a diminution of the rate of conversion until, at a certain concentration, the reaction ceases. The rate of conversion of cinchonidine into cinchotoxine is less than that of cinchonine under the same conditions of temperature and concentration of acid, the ratio between the mean values of the two rates being 1 : 1·21. E. G.

Nature of the Catalysis in the Conversion of the Cinchona Alkaloids into their Toxines. H. C. Biddle (*J. Amer. Chem. Soc.*, 1915, **37**, 2088—2112).—The nature of the catalysis in the conversion of cinchonine and cinchonidine into cinchotoxine in presence of organic acids is discussed in the light of the data obtained by Biddle and Brauer and by Biddle and Butzbach (preceding abstracts). By plotting the specific rates of reaction against the concentration of the hydrogen ion for solutions of

constant concentration with respect to the non-dissociated organic acid, a regular curve is obtained in which the specific reaction rates change the more rapidly the lower the concentration of the hydrogen ion. The specific rate of the reaction with respect to the alkaloid is directly proportional to the concentration of the univalent alkaloid ion, and is a direct linear function of the concentration of the non-dissociated organic acid. The specific catalytic action of the organic acids increases in the order formic, acetic, and propionic. The specific rate of reaction decreases slowly with increasing concentration of the alkaloid. The mean ratio between the specific rates of reaction of the two alkaloids under the same conditions has been shown (preceding abstract) to be 1 : 1·21; this difference seems to be entirely due to the stereoisomeric difference existing between the alkaloids.

These results establish the fact that a non-dissociated molecule can act as a direct catalytic agent in a homogeneous solution.

It is suggested that the conversion of the tertiary alkaloid into cinchotoxine, which contains a secondary nitrogen atom, may be due to the formation of an acetyl or other acyl derivative of cinchotoxine as an intermediate product. E. G.

Properties of Elements and the Periodic System. Nilratan Dhar (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 384—398).—It is shown that the specific cohesion, the temperature-coefficients of the electric and thermal conductivity, the torsional rigidity, Young's modulus and their temperature-coefficients, the specific heat at about 50° (absolute), the coefficient of linear expansion, and the magnetic rotatory power of the elements show a periodic variation when these properties are considered in reference to the atomic weights. H. M. D.

Construction of Compound Molecules with Theoretical Atoms, especially the Systems of Growth of the Organic Compounds of Carbon and Hydrogen. Albert C. Crehore (*Phil. Mag.*, 1915, [vi], **30**, 613—623).—A theoretical paper in which the equations, previously obtained by the author (*ibid.*, 1915, [vi], **29**, 750) for the mechanical force with which one atom acts on another, are applied to the consideration of the configuration of the molecules of the hydrocarbons. The equilibrium positions of the atoms may be found from these equations for the fields of force, but this method becomes impracticable with complex groups of atoms, and a graphical method is described by means of which it has been possible to obtain approximate solutions of the simultaneous equations involved, and so to ascertain the various ways in which the hydrocarbon molecules may be built up.
H. M. D.

Electronic Conception of Positive and Negative Valences. Harry Shipley Fry (*J. Amer. Chem. Soc.*, 1915, **37**, 2368—2373).—A reply to Brunel (this vol., ii, 332). It is contended that Brunel's criticisms and conclusions have little, if any, bearing on

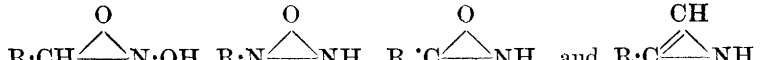
the electronic conception of positive and negative valences as a formulative hypothesis (compare Fry, A., 1911, i, 431; 1912, ii, 546, 713; 1913, ii, 363; 1914, i, 263, 675; this vol., i, 391).

E. G.

Valency of the Elements. II. Simple Organic Nitrogen Compounds. G. Povarnin (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 989—1036. Compare this vol., ii, 548).—The author applies his theory of polar affinities to explain the structure of nitro-compounds and their reduction products, diazo-compounds, oximes, nitriles, etc. The paper does not admit of abstraction at reasonable length, but attention may be drawn to a few of the points considered.

Against the theory of the valency of nitrogen usually accepted, it is urged that this theory assumes, in nitrogen and the other elements of the fifth group, the property of increasing and diminishing in valency under the influence of various agents, there being no general rule for such changes in valency. In this connexion, the formation of nitro-compounds by treatment of hydrocarbons with nitric acid, in which the nitrogen is quinquevalent, and by treatment of iodo-derivatives with silver nitrite, in which the nitrogen is tervalent, is discussed. The ordinary theory of valency supposes, further, that in *iso*nitro-salts, diazo-compounds and oximes, nitrogen is able to fix groups combined with it in definite structural positions in virtue of some peculiar force of attraction for aromatic radicles. In addition, the structures assigned to azo- and hydrazo-compounds, oximes and hydroxamic acids require intramolecular rearrangements, not merely hydrogen, but also oxygen, nitrogen, and radicles undergoing change of position; the most important of these, namely, Beckmann's, and the semidine and benzidine rearrangements, and those of the azoxy- and diazoamino-compounds, are assumed without any sufficient general theoretical motive. Again, the replacement of hydrogen united to nitrogen by metals in the case of azoaminobenzene, phenylnitroamine, etc., and its non-replacement in the case of *iso*nitriles and oximes, find no explanation in the theory of valency.

Development of the author's theory leads to the conclusion that, in all reactions, more or less labile intermediate products are formed, and that many compounds exist in one or several tautomeric modifications, as well as in isomeric forms. In the chemistry of nitrogen, an important part is assigned to three-membered rings; thus, nitro-compounds, diazo-compounds, oximes, and nitriles are regarded as capable of existing in forms having the following *iso*-structures, respectively:

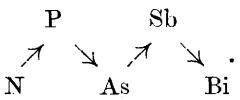


T. H. P.

Phenomena of Secondary Valency. E. V. Biron (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 964—988).—The author's investigations are based on the observation that, with the groups phosphorus, arsenic, antimony; chlorine, bromine, iodine; sulphur, selenium, tellurium, the affinity towards oxygen does not vary continuously in any one period, but is least for the middle element in each case. The results show that, in the sub-groups of the periodic system of the elements, many of the properties of the elements and their compounds vary, not progressively, but periodically as the atomic weight increases. To this phenomenon the name "secondary periodicity" is given.

In the case of the hydrogen haloids, the physical properties and the thermochemical and electrochemical magnitudes for the bromine compound are intermediate to those of the chlorine and iodine compounds. With the oxygen compounds of the halogens, no such regularity exists; for example, bromic acid is less stable, a stronger oxidising agent, and a stronger acid than either chloric or iodic acid.

In the group nitrogen, phosphorus, arsenic, antimony, and bismuth, the properties of the compounds RH_3, RMe_3, REt_3, etc., change progressively with the molecular weight. The conversion of the tervalent atom into the quinquevalent form is easier for phosphorus than for nitrogen or arsenic, more difficult for arsenic than for phosphorus or antimony, and easier for antimony than for arsenic or bismuth; the stability of the quinquevalent type exhibits similar behaviour. Thus, the capacity of the tervalent compounds for conversion into quinquevalent compounds, and also the stability of the latter, are periodic functions of the atomic weight for elements of group V, and may be represented thus:



Further, for these elements the heats of formation of the oxides, (R_2,O_3,Aq), ($R_2,O_3,3H_2O$), (R_2,O_5,Aq), and ($R_2,O_5,3H_2O$), exhibit similar periodicity. Judging from the amplitudes of the periodic variations in the heats of formation of the oxygen compounds of antimony, arsenic, phosphorus, and nitrogen, and those of iodine, bromine, and chlorine, the oxygen compounds of fluorine would be expected to be so endothermic as to be absolutely unstable; to this, apparently, is due the failure to prepare such compounds.

With the non-metals of the sixth group of the periodic system, secondary periodicity is observed with the oxygen compounds. Thus, the heats of formation for (R,H_2) are +2730, −5400, and −32,000 for sulphur, selenium, and tellurium, respectively; for (R,O_2,Aq), 78,780, 56,160, and 77,180; for (R,O_3,Aq), 142,410, 76,660 and 98,380.

An attempt was made to correlate the occurrence of secondary periodicity with Jessup's hypothesis of the evolution and devolution of the elements (A., 1908, ii, 96), it being thought that such

periodicity exists with elements of indirect evolution. This view is, however, contradicted by the fact that secondary periodicity is met with in the alkali metals and in the elements of the zero group, which, according to A. C. and A. E. Jessup, are elements of direct evolution. The data available, although incomplete, indicate, indeed, that secondary periodicity is a general property of the elements.

As regards what properties and what elements exhibit, on the one hand, progressive variation, and, on the other, secondary periodicity, the author finds an explanation in Abegg's theory of twofold valencies (A., 1904, ii, 475). It is found that the elements of sub-groups form triads, the compounds of which exhibit physical and chemical properties (1) varying regularly when the compounds are formed with the normal valencies, and (2) showing secondary periodicity when the compounds are formed with the contra-valencies. A number of cases are given in support of these conclusions.

Consideration of the curves and numerical data given by Rudorf (A., 1905, ii, 69) shows that the magnitude, v/A^2, changes either progressively or periodically with increase in the atomic weight of the elements of a sub-group, periodicity being observed in those sub-groups in which contra-valencies are manifested the more strongly and in which secondary periodicity has been found with other properties. Thus, if v_1 represents the difference between the vibration frequencies of the first and second lines of a triplet, and v_2 the corresponding difference for the first and third lines, the values of $100\ v_1/A^2$ for oxygen, sulphur, selenium, and tellurium are 1·44, 1·77, 1·65, and 1·83 respectively, and those of $100\ v_2/A^2$ for oxygen, sulphur, and selenium, 2·25, 2·85, and 2·35.

T. H. P.

Gas Generator. A. Kleine (*Zeitsch. angew. Chem.*, 1915, **28**, 388).—The apparatus is similar in shape to the ordinary Kipp generator, but its action is entirely different from that of the latter. The upper bulb, or reservoir, which, if desired, may consist of a large bottle fixed on a shelf above the other part of the apparatus, is connected by a tapped tube with the middle bulb, the latter containing the solid substance (marble, zinc, ferrous sulphide, etc.) from which the gas is to be generated. The solution from the reservoir is allowed to fall, drop by drop, on to the substance in the middle bulb, and the gas evolved is drawn off through a side-tube on this bulb. The exhausted solution, collecting at the bottom of the middle bulb, passes through a short siphon into the lowermost bulb, from which it is run off when necessary. When the supply of gas is no longer needed, the evolution is stopped by closing the tap on the tube leading to the reservoir. W. P. S.

Apparatus for the Study of Reactions between Gases and Liquids. E. Emmet Reid (*J. Amer. Chem. Soc.*, 1915, **37**, 2112—2114).—Apparatus is described which was devised for use in experiments on catalytic hydrogenation, and is applicable to

the study of any reaction between gases and liquids. It consists of a flask with inlet and outlet tubes for the gas, a stirrer run by an electric motor, and a special device for rendering the apparatus gas-tight for both increased and diminished pressure. This device passes through the cork in the neck of the flask, and consists of a double steel bearing with a central cavity filled with mercury, forming a mercury seal, which does not offer any resistance to the motion of the shaft to which the stirrer is attached. The apparatus has been used for temperatures up to 220°, and the stirrer has been run without difficulty at speeds of 3300—4000 revolutions per minute. E. G.

Convenient Weighing Pipette. FRANK HALL (*J. Amer. Chem. Soc.*, 1915, **37**, 2062—2063).—A form of pipette is described which is easily filled and cleaned, can be conveniently weighed, and is not fragile. It consists of an ordinary pipette bulb with a short tube below provided with a stopcock and a short, thick-walled tube above with a small bulb in it. The object of this small bulb is to serve as an overflow reservoir on filling the pipette, and also to prevent the tube from slipping through the hook by which the pipette is suspended from the arm of the balance. The hook is made of a piece of sheet metal, and is provided with a slot large enough to admit the tube, but too narrow to allow the bulb to pass through. E. G.

Simple Ball Mill for Laboratory Use. A. COBENZL (*Chem. Zeit.*, 1915, **39**, 708).—A globular separating funnel is mounted horizontally on two bearings, one holding the neck and the other the stem. The substance to be ground is placed in the funnel together with a number of glass or metal balls, and the apparatus is rotated by means of a pulley fixed on the stem. W. P. S.

Inorganic Chemistry.

Theory of Water Vapour. K. J. Mostovitsch (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1144—1159).—A mathematical paper. Following Nernst's hypothesis, according to which superheated water-vapour consists of a mixture of two ideal gases, H_2O and $(H_2O)_2$, the author calculates the degree of dissociation, x, and the value of the equilibrium constant, K_p, of the reaction, $2H_2O \rightleftarrows (H_2O)_2$, for various temperatures and for $p=1$ or 10 atmospheres. At the absolute temperature, 678°, the second member of Linde's empirical expression for superheated water-vapour,

$$pv=47{\cdot}1T-p(1+0{\cdot}02p)[0{\cdot}031(373/T)^3-0{\cdot}0052],$$

vanishes, the vapour at this temperature beginning to follow strictly

the law of ideal gases, and x having the value 1; since the approach of a gas to the ideal state is asymptotic, Linde's equation is regarded as inaccurate. For the value of the heat, Q_v, of the dissociation, $(H_2O)_2 = 2H_2O$, the expression, $Q_v = 0{\cdot}021T + 0{\cdot}021T^2$, is obtained, the value at 100° being 2925 cal. per gram-mol., and that of Q_p 3420 cal. Nernst's hypothesis leads to values for the heat of evaporation at different pressures in good agreement with the observed values. For pressures lying between 1 and 20 atmospheres, the value of x for any values of p and T is given by the expression:

$$x = \sqrt{[10^{a+b(T-T_3)}/p + 10^{a+b(T-T_3)}]},$$

where T is the temperature of saturation, and a and b have the respective values 1·20140 and 0·00535. T. H. P.

Apparatus for Rapidly Testing Substances Used Against Poisonous Gases. E. KOHN-ABREST (*Compt. rend.*, 1915, **161**, 310—313).—A simple piece of apparatus is sketched, and described, by means of which a definite volume of a mixture of air and poisonous gases can be slowly aspirated over a plug of cotton-wool, charged with a solution of the absorbing agent to be tested. A number of materials have been tested, the volume of gaseous mixture used in each case being 250 c.c., slowly aspirated at about the same rate as the inspiration of air during breathing. The poisonous gas used was chlorine, and for mixtures containing 1 in 1000 or less of this gas, cotton-wool alone, either wet or dry, was sufficient to absorb it all. Only when the chlorine rose to above 1% was any difference noticeable among the absorbing agents used. With concentrations greater than 1% a saturated solution of sodium carbonate absorbs the chlorine very energetically. Solutions of sodium hydrogen carbonate are only moderate. When sodium thiosulphate is used, sulphur dioxide is liberated, and in its turn requires sodium carbonate for its absorption. The addition of glycerol to the absorbent solutions serves mainly to prevent evaporation, and it also produces a more uniform absorption of the chlorine. W. G.

Action of Bromine on Alkali Iodides. WILLIAM NORMAN RAE (T., 1915, **107**, 1286—1291).—When bromine vapour is allowed to act on dry ammonium iodide, the solid at first turns black, due to the liberation of iodine. Further action of bromine causes it again to change its colour to a brilliant red. The red compound is shown to be ammonium bromoiodobromide, $NH_4{\cdot}BrIBr$ (compare Jackson and Derby, A., 1900, ii, 596). Time-absorption curves were made, showing the rate of absorption of bromine in this preparation, and from them it is deduced that poly-haloids of the type $MIBr_4$, corresponding with the well-known compounds $MICl_4$, cannot exist, since the absorption of bromine ceases entirely when the compound NH_4IBr_2 has been formed. Further, it seems unlikely that IBr_3 exists. Ammonium bromoiodobromide can be prepared in large, ruby-red prisms, which are green by reflected light, when the calculated quantities of ammonium bromide, iodine, and bromine are dissolved in a small quantity of water, and the

solution concentrated over phosphoric oxide in a desiccator. When heated, it loses iodine bromide, and leaves ammonium bromide, and when washed with ether ammonium bromide remains behind.

The rate of decomposition of cæsium pentaiodide and cæsium tetrachloroiodide was studied by allowing these compounds to remain in a desiccator over potassium hydroxide and plotting the loss in weight against the time. It is shown that breaks occur in the curves which correspond with the compounds cæsium tri-iodide and cæsium dichloroiodide. These two compounds were isolated and analysed. The former loses iodine very slowly at 28°, but rapidly at 63°, leaving cæsium iodide; the latter compound is fairly stable at 28°, but loses iodine rapidly at 118°, and leaves cæsium chloride.

The action of bromine vapour on the iodides of sodium, potassium, rubidium, and cæsium was next investigated. In the case of the three last-named iodides, compounds were formed similar to that produced with ammonium iodide, but no such compound was formed with sodium iodide. These compounds have the general formula M·BrIBr, and are all bright red powders.

When a polyhaloid containing two or more different halogen atoms is decomposed, either by heating or spontaneously, the residue always contains the halogen of lowest atomic weight. From this it is deduced that the halogen of smallest atomic weight is attached to the metal by its principal valency, and to the other halogen atoms by subsidiary valencies. J. F. S.

Internal Temperature of Sulphur Furnaces. Stefano Pagliani (*Ann. Chim. Applicata*, 1915, **4**, 75—81).—The theoretical temperature at which sulphur burns in the calculated proportion of air is found to be 1616° at constant pressure and 2000° at constant volume. When, however, the combustion takes place in the normal proportion of air used in sulphuric acid works, this theoretical temperature is 900°, whilst the maximum temperature encountered in practice in furnaces working normally is 550°. In combustion furnaces for the extraction of sulphur from its minerals, the temperature should not be below 250°, which is the minimum temperature at which sulphur burns in a large excess of air. The incomplete utilisation of the sulphur in these furnaces is due partly to the large volumes of air required to prevent the temperature rising beyond 300—340°, above which temperature the sulphur becomes mobile again. T. H. P.

Reduction of Nitric Oxide by Contact Action of Metals and Metallic Oxides. Birendra Bhusan Adhikary (*Chem. News*, 1915, **112**, 163—164).—The hydrogenation of nitric oxide is brought about by the catalytic action of various metals at elevated temperatures, an important determining factor being the state of division of the catalyst. Thus gold, silver, or lead in the form of foil are almost inactive, but the freshly reduced metals in the form of powder give large quantities of ammonia when a mixture of nitric oxide and hydrogen in the ratio 1 : 3 is passed over them.

Gold acts best at 335—345°, and silver at 430°. Zinc dust, reduced iron, and powdered tin give almost quantitative yields of ammonia, whilst magnesium, mercury, and aluminium are inactive. Antimony and bismuth when freshly reduced from their oxides also exert a catalytic action. Certain oxides which are reducible under the conditions of the reaction act equally well as catalysts, for example, the oxides of zinc, lead, cadmium, tin, bismuth, antimony, chromium, and manganese. Oxides of barium, aluminium, magnesium, mercury, boron, silicon, and arsenic, on the other hand, are inactive. G. F. M.

Densities and Degrees of Dissociation of the Saturated Vapour of Phosphorus Pentachloride. Alexander Smith and Robert H. Lombard (*J. Amer. Chem. Soc.*, 1915, **37**, 2055—2062).—The observations published hitherto on the vapour densities of phosphorus pentachloride refer to the unsaturated vapour. Determinations have now been made at temperatures from 90° to 160° of the vapour densities of the saturated vapour in equilibrium with the solid phase by a modification of the method employed by the authors in their work on the ammonium haloids (this vol., ii, 86).

The degrees of dissociation calculated from the vapour densities show that the saturated vapour is somewhat associated at 90°, and is dissociated to an approximately constant extent of about 4% between 110° and 160°. The latent heat of vaporisation was calculated, and found to be 15,500 cal. per mol.

The statement that ammonium iodide is partly associated in the saturated vapour (*loc. cit.*) has been confirmed. E. G.

Coagulation of Arsenious Sulphide Sol by Electrolytes. Jnanendranath Mukhopadhyaya (*J. Amer. Chem. Soc.*, 1915, **37**, 2024—2031).—A study of the coagulation of colloidal solutions of arsenious sulphide has led to the following conclusions. The stability of arsenious sulphide sols increases with the dilution, but fine sols are less stable than coarse sols of the same concentration. Coagulation of colloidal arsenious sulphide by the action of electrolytes is due mainly to the coalition of the colloidal particles, and very little to sedimentation. The rate of coalition depends on the concentration and nature of the electrolyte. With concentrated sols and dilute electrolytes, the coagulation proceeds by stages until the colloid has separated completely. Hydrogen sulphide renders the colloidal solutions much more stable towards electrolytes. Electrolytes are not adsorbed to any marked extent by the colloid. E. G.

Equilibrium Between Carbonyl Sulphide, Carbon Monoxide, and Sulphur. Gilbert N. Lewis and William N. Lacey (*J. Amer. Chem. Soc.*, 1915, **37**, 1976—1983).—The free energy of formation of sulphur dioxide cannot be obtained directly from the free energy of the reduction of sulphur dioxide to sulphur by carbon monoxide, since the conditions of equilibrium in this reaction are complicated by the formation of carbonyl sulphide.

A study of these reactions has therefore been made, and has shown that when carbon monoxide and sulphur are heated together at 250—300°, carbonyl sulphide, carbon dioxide, carbon disulphide, and carbon monosulphide are formed, thus: (1) $CO+S=COS$; (2) $2COS=CO_2+CS_2$; (3) $CS_2=CS+S$. The equilibrium constant, $K=[COS]/[CO]$, was found to be 201 at 302°, and approximately 435 at 260°. The equilibrium constants of the other two reactions were also estimated approximately. E. G.

Formation of Carbonates of the Alkali Metals. P. Melikov and M. Rozenblat (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1093—1094).—In the estimation of alkali metals in the form of chlorides, these are often heated with excess of ammonium carbonate. The authors find that, when ammonium carbonate is added gradually to fused sodium or potassium chloride in a platinum crucible, sodium or potassium carbonate is formed in amount depending on the quantity of ammonium carbonate added. The reaction, $2NaCl+(NH_4)_2CO_3 \rightleftarrows Na_2CO_3+2NH_4Cl$, is reversible, and if ammonium carbonate and chloride are added together to the fused chloride, no formation of sodium carbonate takes place. Fused sodium or potassium sulphate gives no corresponding carbonate when treated with ammonium carbonate. T. H. P.

Reaction Between Sodamide and Hydrogen. F. D. Miles (*Proc. Roy. Soc. Edin.*, 1915, **35**, 134—137).—When sodamide is heated in a stream of hydrogen at temperatures between 200° and 300° a reaction occurs in which a portion of the sodamide is converted into sodium hydride with liberation of ammonia according to the equation $NaNH_2+H_2=NaH+NH_3$. This reaction does not appear to take place when sodamide is heated with hydrogen in an enclosed space up to 300° (compare Titherley, T., 1894, **65**, 509). J. F. S.

New Crystalline Variety of Silver. Tarini Charan Choudhri (*J. Amer. Chem. Soc.*, 1915, **37**, 2037—2039).—When spongy silver, prepared by igniting silver tartrate, is treated with nitric acid (D 1·42) which has been freed from the lower oxides of nitrogen by heating it with carbamide, some action takes place at first with formation of silver nitrate and nitrous acid, but this action ceases after a time, and if the mixture is left for two weeks with occasional shaking, long, needle-shaped crystals are gradually produced. This is regarded as a new variety of crystalline silver, belonging to the cubic system. E. G.

The Solubility of Silver Oxide in Water. G. Rebière (*Bull. Soc. chim.*, 1915, [iv], **17**, 309—312).—Four different samples of silver oxide were prepared, and their solubilities determined in distilled water at 25° and 50°. The samples were prepared (1) by the action of sodium hydroxide, freshly prepared by the solution of sodium in water, on a dilute solution of silver nitrate; (2) by the action of aqueous barium hydroxide on silver nitrate; (3) by the

action of concentrated sodium hydroxide on moist, freshly precipitated silver chloride; (4) by the same reagent and moist, freshly precipitated silver carbonate. The silver oxide was shaken with distilled water in a thermostat for two hours, the solution filtered, the first portion rejected, and the silver estimated in 100 c.c. of the filtrate by the method already described (this vol., ii, 797). The results obtained vary somewhat for the different samples, that for the first sample, $2{\cdot}16 \times 10^{-4}$ gram-molecules per litre, being in exact agreement with the values obtained by Noyes and Kohr (compare A., 1903, ii, 201) and Böttger (compare A., 1904, ii, 241).

W. G.

Determination of the Solubility of Silver Nitrite and its Degree of Dissociation in a Saturated Solution. Henry Jermain Maude Creighton, and William Hillis Ward (*J. Amer. Chem. Soc.*, 1915, **37**, 2333—2338).—The conductivity of silver nitrite solutions at 25° has been determined, and the results indicate that the salt suffers hydrolysis. The percentage solubility of silver nitrite has been determined as follows: at 1°, 0·1589; at 15°, 0·2752; at 25°, 0·4135; at 35°, 0·6016; at 51°, 1·0240; and at 60°, 1·3625. The addition of silver or nitrite ions at 25° reduces the solubility of silver nitrite; equimolar quantities of these ions cause approximately the same decrease. Calculations of the solubility of silver nitrite in presence of different quantities of silver nitrate show that the degree of dissociation of the nitrite in a saturated solution is much greater than that indicated by conductivity measurements. From the results of the solubility determinations the degree of dissociation of silver nitrite in a saturated solution at 25° has been found to have a mean value of 0·90, whence the solubility product is $5{\cdot}86 \times 10^{-4}$ at 25°. E. G.

Solubility Product Constant of Calcium and Magnesium Carbonates. John Johnston (*J. Amer. Chem. Soc.*, 1915, **37**, 2001—2020).—The solubility product constants of calcium carbonate (calcite), magnesium carbonate, $MgCO_3,3H_2O$, and barium carbonate have been recalculated from existing data, with the following results: $[Ca^{\cdot\cdot}][CO_3''] = 0{\cdot}98 \times 10^{-8}$ at 16° when the solution is saturated with respect to calcite; $[Mg^{\cdot\cdot}][CO_3''] = 1{\cdot}93 \times 10^{-4}$ at 12°, the solution being saturated with magnesium carbonate;

$$[Ba^{\cdot\cdot}][CO_3''] = 7 \times 10^{-9}$$

at 16°, the solid phase being barium carbonate, $BaCO_3$. The solubility product constant, K_{Mg}, of magnesium carbonate at temperatures up to 50° is given by the formula $\log K_{Mg} = 2315/T - 11{\cdot}870$, whence the heat of the reaction $MgCO_3,3H_2O = Mg^{\cdot\cdot} + CO_3'' + 3H_2O$ is +10,600 cal.

By the aid of these data and that of the solubility product constant of magnesium hydroxide, it is shown that calcium carbonate precipitated from solutions containing magnesium is liable to contain small quantities of magnesium hydroxide, which can only be slowly removed by the ordinary method of reprecipitation; that, on precipitating magnesium by means of carbonates, mixtures of

magnesium carbonate and hydroxide will be obtained, and that both calcium and magnesium carbonates can be prepared free from contamination by keeping the partial pressures of carbon dioxide above a certain limiting value. E. G.

Water of Crystallisation. II. Compounds with $2H_2O$. I. Guareschi (*Atti R. Accad. Sci. Torinò*, 1915, **50**, 881—902).—The author has examined a number of other salts (compare A., 1914, ii, 459), the principal results being as follows.

The temperature of dehydration of dihydrated calcium sulphate is not 130°, as stated by Rosenstiehl (A., 1911, ii, 386), but 93—94°, or, in a current of dry air, 81—82°, these temperatures being valid for both the natural and the precipitated salts; the former, however, loses immediately a large proportion of its water when heated in a current of dry air, whereas the latter exhibits only a slight loss after some hours. The semi-hydrated sulphate is probably to be regarded as of the formula $Ca_2S_2O_8,H_2O$.

Dehydrated sodium nitroprusside rapidly absorbs $2H_2O$ from the air, and the hydrate thus obtained undergoes complete dehydration much more easily than the original hydrate, the temperature of dehydration being 98—99°. The final $\frac{1}{2}H_2O$ is removed only slowly and with difficulty, the probable formula of the salt being $[Na_2Fe(NO)(CN)_5]_2,4H_2O$.

Cupric chloride is completely dehydrated at 55° in a current of dry air, or at 15° over sulphuric acid at a pressure of 10 mm. Sodium bromide loses both mols. of water in an oven at 30°, the first rapidly and the second more slowly. Sodium iodide undergoes complete dehydration in seven to eight days over sulphuric acid at 15—17°. Cadmium acetate loses $1\frac{3}{4}H_2O$ rapidly in a steam oven, and the remainder slowly, its formula being probably a multiple of the simple one; its dehydration temperature is 50°. Potassium ethane-$\alpha\alpha$-disulphonate loses $1H_2O$ rapidly, and the remaining $1H_2O$ very slowly in an oven at 30°. Sodium dithionate is dehydrated at 50° in an oven or at 42° in a current of dry air, the final $1H_2O$ being removed only very slowly. The dehydration point of barium dithionate is 50° in an oven or 30° in a current of dry air; the structure $Ba<^{O\cdot SO(OH)_2}_{O\cdot SO(OH)_2}$ is suggested for this salt.

T. H. P.

Lower Compounds of Certain Elements. L. Marino (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 143—149).—The results of many recent applications of the laws of chemical equilibrium to the study of the relations existing between the different degrees of oxidation of an element, or between an element and its typical compounds, indicate the existence of compounds in which the valency of the element is lower than its ordinary value. In some of these cases, however, the failure to consider the influences of various factors which mask the principal phenomenon has led to erroneous conclusions. The two particular instances considered by the author are calcium subhydride, CaH, and barium subchloride, BaCl.

In the course of their measurements of the dissociation pressure of calcium hydride, Moldenhauer and Roll-Hansen (A., 1913, ii, 705) found that, when one-half the quantity of hydrogen required to give the normal hydride has been absorbed by calcium, the pressure curve undergoes change in direction. Repetition of this work by the author and Quinto gives results which are in moderately good agreement with those of the above-named authors, and are to be published in detail. When, however, an attempt is made to construct the curve representing the dissociation of calcium subhydride, it is found that part of the hydrogen has escaped measurement. This phenomenon has been traced to the volatility of the calcium. As the temperature is raised, dissociation proceeds in accordance with the equilibrium, $CaH_2 \rightleftarrows Ca + H_2$, but at temperatures below 800° a little of the calcium is condensed in the part of the quartz-containing tube which is somewhat less strongly heated. In this cooler space, the liberated hydrogen is fixed by the calcium in correspondence with the dissociation pressure of the hydride at the lower temperature. A method has been devised of determining the distribution of the hydrogen in the various parts of the apparatus, and the new pressure curve thus obtained fails to indicate the presence of a new compound. These results show that it is inaccurate to speak of the heats of combination of the first and second atoms of hydrogen with calcium, and afford an explanation of the divergence of the value of the heat of combination determined calorimetrically from that calculated by means of Nernst's formula.

Guntz's results (A., 1903, ii, 369), and also those of Haber and Tolloczko (A., 1904, ii, 813; *Ann. Physik*, 1908, **26**, 935), are compatible with the view that the supposed barium subchloride, or compounds such as BaCl, NaCl, are solid solutions of barium or sodium in ordinary barium chloride. On the other hand, these sub-compounds may result from metallic pulverisation in the crystals of barium chloride similar to those observed by Lorenz and Eitel (this vol., ii, 260, 261). T. H. P.

Atomic Weight of Cadmium. G. A. Hulett and E. L. Quinn (*J. Amer. Chem. Soc.*, 1915, **37**, 1997—2000).—Baxter and Hartmann in a paper on the atomic weight of cadmium (this vol., ii, 98), referred to the work of Perdue and Hulett (A., 1911, ii, 397), Laird and Hulett (*Trans. Amer. Electrochem. Soc.*, 1912, **22**, 385), and Quinn and Hulett (A., 1914, ii, 127), and pointed out some possible sources of error which might account for the lower values for the atomic weight obtained by these authors. The present paper is a reply to these criticisms. E. G.

Reactions between Potassamide and Certain Salts of Cadmium, Nickel, and Chromium in Solution in Liquid Ammonia. George S. Bohart (*J. Physical Chem.*, 1915, **19**, 537—563).—The action of potassamide on solutions of cadmium iodide, potassium cadmium cyanide, potassium nickel cyanide, nickel thiocyanate, and ammonium chromium thiocyanate in liquid

ammonia has been studied. A detailed account of the method of manipulation of liquid ammonia solutions is given in the paper. When either of the above-mentioned cadmium salts is treated with a solution of potassamide in liquid ammonia, cadmium amide or potassium cadmium amide is formed accordingly as the ammonio-base or the salt is in excess. *Cadmium amide*, $Cd(NH_2)_2$, is a white powder, which on exposure to moist air assumes an orange colour, and then slowly changes to pure, white cadmium hydroxide. It reacts violently with water, and when suddenly heated explodes, with the liberation of metallic cadmium. When heated at 180° in a vacuum, it loses ammonia and leaves cadmium nitride, Cd_3N_2, a black, amorphous powder, which becomes orange-coloured on exposure to moist air, and then slowly becomes white. It explodes violently when brought into contact with water, and deposits metallic cadmium. *Potassium cadmium amide*, $Cd(NHK)_2,2NH_3$, is a white, flocculent powder, which becomes grey when exposed to light. It reacts violently with water, producing ammonia, potassium hydroxide, and cadmium hydroxide.

Potassium nickel cyanide, $2KCN,Ni(CN)_2$, yields three distinct compounds when treated with a solution of potassamide in liquid ammonia. (1) With excess of the salt. A brownish-red, slightly soluble, crystalline substance is obtained, which has the formula $Ni_3N_2H_2K_4(CN)_6,8NH_3$; when these crystals are kept at ordinary temperature and pressure, eight molecules of ammonia escape, and a straw-yellow powder, $Ni_3N_2H_2K_4(CN)_6$, remains. (2) With equivalent amounts of salt and ammonio-base, a lemon-yellow, curdy precipitate is formed; this, when washed with liquid ammonia, crumbles to a heavy powder, having the composition $K(CN)_2Ni{\cdot}NHK$. (3) With a large excess of potassamide, a deep red solution is produced, which, after twelve hours, deposits deep red crystals of the compound $Ni_3N_{11}H_{22}K_7(CN)_2$. The constitution of this salt is not determined, but a number of possible alternative constitutions are suggested. By varying the concentration of ammonia in ammonium hydroxide solutions of nickel thiocyanate, crystalline ammonia derivatives of nickel thiocyanate with 2, 3, 4, and $5\frac{1}{2}$ molecules of ammonia were prepared, and a fifth compound, with $8\frac{1}{2}$ molecules of ammonia, was prepared by removing the liquid phase from a solution of nickel thiocyanate in liquid ammonia at $-40°$. The compound, $Ni(CNS)_2,2NH_3$, is a greenish-blue, vitreous substance which is decomposed by water. The crystals were unsuitable for crystallographic measurement. $Ni(CNS)_2,3NH_3$ is a deep blue, vitreous substance which is decomposed by water; it crystallises in orthorhombic bipyramids. $Ni(CNS)_2,4NH_3$ is a sapphire-blue, vitreous substance which is decomposed by water. It crystallises in monoclinic prisms. It is very soluble in liquid ammonia, and 60 grams dissolve in 100 c.c. of concentrated aqueous ammonia at 18°. The crystals lose their lustre in moist air.

$Ni(CNS)_2,5\frac{1}{2}NH_3$ forms tabular, blue crystals, which have a violet tone; it is similar to the tetra-ammonia derivative in respect

to its solubility, and loses ammonia immediately on exposure to air.

$Ni(CNS)_2,8\frac{1}{2}NH_3$ is similar to the last-mentioned compound. At $-40°$ its vapour tension is 75 mm., and at ordinary temperatures it loses ammonia very rapidly, and forms the compound with $5\frac{1}{2}$ molecules of ammonia.

A solution of nickel thiocyanate in liquid ammonia gives a precipitate of nickelamide when treated with an equivalent amount of potassamide solution. *Nickelamide*, $Ni(NH_2)_2$, is a red, flocculent mass which reacts mildly with water, producing nickel hydroxide and ammonia. When heated at 120° in a vacuum, it yields nickel nitride, Ni_3N_2, a black, amorphous substance which reacts extremely slowly (if at all) with water and dissolves slowly in mineral acids. At 120° it is decomposed into its constituents. Nickelamide dissolves in an excess of potassamide solution, producing a deep red solution, which deposits a red, crystalline substance, *ammonio-potassium nickelamide*, $Ni_2N_3K_5,6NH_3$. It reacts violently with water.

Ammonium chromium thiocyanate, $NH_4Cr(SCN)_4,2NH_3$, in liquid ammonia solution forms at least four different compounds when treated with potassamide. These compounds are, respectively, wine-red, salmon-pink, and purple flocculent precipitates, and a wine-red, crystalline substance. The composition has not been determined. J. F. S.

Allotropic Modification of Lead. Henry Jermain Maude Creighton (*J. Amer. Chem. Soc.*, 1915, **37**, 2064—2065).—Heller (this vol., ii, 634) has described a grey, allotropic modification of lead obtained by leaving ordinary lead in a solution of lead acetate acidified with nitric acid. It has now been found that a similar result is produced when a current is passed through an electrolyte of nitric acid (D 1·42), using a piece of sheet lead as the cathode and a piece of platinum foil as the anode. After eight hours the surface of the lead cathode becomes grey, soft, and powdery. E. G.

The Reciprocal Solubility of Copper and Lead. B. Bogitch (*Compt. rend.*, 1915, **161**, 416—419. Compare Heycock and Neville, A., 1897, ii, 245; Friedrich and Leroux, A., 1907, ii, 620).—When copper and lead are melted together they form a double layer when the amount of copper exceeds 34·5% and is less than 87%. This double liquid layer can only exist between 940°, the solidification temperature of the upper layer, and 975°. Above the latter temperature there is no indication of any difference in composition throughout the liquid mass. W. G.

Equilibria in the System Cu–S–O; the Roasting Reaction Process with Copper. W. Reinders and F. Goudriaan (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 150—165).—An attempt has been made to elucidate the mechanism of the roasting processes connected with the metallurgy of copper by a determination of

the pressure of the sulphur dioxide which is in equilibrium with various combinations of intermediate products. Tables are given showing the equilibrium pressures at various temperatures corresponding with the following systems:—$2Cu_2O + Cu_2S \rightleftarrows 6Cu + SO_2$; $3CuS + CuSO_4 \rightleftarrows 2Cu_2S + 2SO_2$; $Cu_2S + 2CuSO_4 \rightleftarrows 2Cu_2O + 3SO_2$; $4CuSO_4 + Cu_2O \rightleftarrows 3(CuO,CuSO_4) + SO_2$; $CuO,CuSO_4 + Cu_2O \rightleftarrows 4CuO + SO_2$; $2CuSO_4 \rightleftarrows CuO,CuSO_4 + SO_3$; and $CuO,CuSO_4 \rightleftarrows 2CuO + SO_3$. H. M. D.

Action of Potassium Hydroxide on Atacamite. S. Tschumanov (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1268—1269).—The hydrate (1) $7CuO,H_2O$, is obtained by addition of potassium hydroxide solution to cupric chloride solution; (2) $8{\cdot}5CuO,H_2O$, by addition of cupric chloride solution to potassium hydroxide solution; $7CuO,H_2O$ and $4CuO,H_2O$, by addition of potassium hydroxide solution to copper sulphate solution and atacamite respectively, all at the ordinary temperature. If the hydrates (1) and (2) are heated at 100° after precipitation and are washed with boiling water, they assume the respective compositions $9CuO,H_2O$ and $7CuO,H_2O$. T. H. P.

Interaction of Atacamite and Ammonium Bromide. S. Tschumanov (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1269—1272).—Atacamite enters into reaction with ammonium nitrate, sulphate, bromide or iodide, silver nitrate, or mercuric chloride, when shaken for some days with a concentrated aqueous solution of one of these salts. This action is most rapid with ammonium iodide and bromide. In the latter case an insoluble, crystalline product is obtained, which has a composition corresponding approximately with the formula

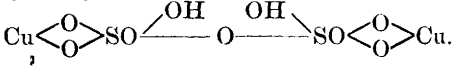
$$[Cu\begin{pmatrix}NH_4\\NH_4\end{pmatrix}Cu)_3Br_2],10NH_4Br,$$

and readily loses ammonium bromide when treated with water. T. H. P.

Water of Crystallisation. III. Compounds with $5H_2O$. Copper Sulphate. Icilio Guareschi (*Atti R. Accad. Sci. Torino*, 1915, **50**, 1125—1145. Compare this vol., ii, 770).—Over calcium chloride at 21—23° pentahydrated copper sulphate loses only $2H_2O$, yielding the pale sky-blue trihydrate, which loses $2H_2O$, forming the monohydrate in a thermostat at 60°, or, if left in the air, is re-converted into the pentahydrate. The latter undergoes no change at 40°, but loses $2H_2O$ at 45—50°, a further $2H_2O$ at 60°, and the final $1H_2O$ at 206°. In a current of dry air at 41—42°, $CuSO_4,5H_2O$ loses $1\frac{1}{2}H_2O$ in five hours, and another $\frac{1}{2}H_2O$ in a second period of five hours; no further loss then occurs at 50—60°, but at 72° $2H_2O$ is removed, the monohydrated salt remaining. Pierre's statement (*Ann. Chim. Phys.*, 1846, [iii], **16**, 241, 250), that pentahydrated copper sulphate crystallised at temperatures above 25° is dehydrated completely in a current of dry air at 114°, is inaccurate, $1H_2O$ remaining at this temperature. At

206—207°, $CuSO_4,5H_2O$ loses $4H_2O$ in less than half-an-hour, a further $\frac{1}{2}H_2O$ being removed very slowly, and the last $\frac{1}{2}H_2O$ more slowly still.

The doubled formula is assumed for copper sulphate, the monohydrate (semihydrate) being represented thus:



T. H. P.

Electrolysis of Solutions of the Rare Earths. II. L. M. DENNIS and P. A. VAN DER MEULEN (*J. Amer. Chem. Soc.*, 1915, **37**, 1963—1976).—Dennis and Lemon (this vol., ii, 99) have described a method of fractional electrolysis of neutral solutions of the nitrates of the rare earths, in which a mercury cathode and platinum anode were employed. As a diaphragm was not used, it seemed possible that the fractional precipitation of the hydroxides of the rare earth metals might have been caused by ammonia formed by the cathodic reduction of the nitric acid. In order to ascertain whether a fractional separation could be effected under conditions in which ammonia could not be present, a solution of the rare-earth chlorides was submitted to electrolysis. The material employed consisted of the oxides of the yttrium group from which cerium and nearly all the didymium had been removed. On fractional electrolysis of the chlorides of these earths, the coloured earths concentrated in the earlier fractions and yttrium in the later fractions, a little neodymium which was present appearing in the last fractions. Fractional electrolysis, with the use of a diaphragm, of the nitrates of these earths, gave similar results, but the rate of precipitation was about four times as great as from the chlorides; ammonium salts were not produced in this experiment. In six fractions obtained from a solution, rich in erbium, holmium, thulium, and yttrium, the first three metals were not appreciably separated from one another, but were rapidly separated from the yttrium. Under the conditions of these experiments the hydroxides of the rare earths are precipitated in the order of their basicities. E. G.

The Rare Earths. I. CH. GARNIER (*Arch. Sci. phys. nat.*, 1915, [vi], **40**, 93—105 and 199—213).—After a description of the general characteristics and methods of separation of the rare earths the author describes a series of experiments on neodymium. A quantity of commercial neodymium salt containing traces of praseodymium and samarium was purified by means of fractional crystallisation of the nitrobenzenesulphonate (Holmberg, A., 1907, ii, 90), since this method is found to be the most efficient and speedy. In this way fifteen final fractions were obtained, and of these the first and the last two were discarded. The remaining twelve fractions were converted into the chloride, and the absorption spectrum of each examined in $N/8$-aqueous solutions 200 mm. thick. The wave-lengths of the bands found are given in the paper for the alternate fractions. There is very little difference shown by the

various fractions. The atomic weight has also been determined for the material in fractions 4, 5, and 6. The fourth fraction yields a value 144·6, and the fifth and sixth give a value 144·4. Fractions 5 and 6, which in the author's opinion are free from praseodymium, have been used in the study of the hydrates and oxide of neodymium described below. The colour of neodymium oxide has been variously described as blue, ash-grey, green, blue with a violet tone, pale violet, lavender, nearly white with a tinge of bluish-grey, and finally Waegner states (A., 1905, ii, 35) that the colour depends, not only on the purity of the substance, but also on the method of preparation. He obtains the oxide rose-brown, blue, and rose coloured. From the method of preparation the author draws the conclusion that the difference in colour of Waegner's oxides is not due to difference in the amount of oxygen contained, as is claimed, but rather to a difference in the degree of hydration. To confirm this view, neodymium hydroxide, $Nd(OH)_3$, has been heated at various temperatures in an electric furnace in a current of nitrogen, and the loss of water controlled. It is thus shown that two hydrates in addition to the normal hydroxide exist. The first of these, $2Nd_2O_3,3H_2O$, is formed at 320°, and is stable up to 520°. It has a light brown colour tinged with rose, and apparently corresponds by its reflexion spectrum with the similarly coloured oxide of Waegner (*loc. cit.*). The second hydrate, Nd_2O_3,H_2O, has a less pronounced colour than the first-mentioned product, and is stable between 520° and 580°, and is shown to be identical with the substance regarded by Waegner as Nd_4O_7. This hydrate on further heating passes directly into the blue sesquioxide, and the colour changes slowly as the temperature increases, passing through the shades mentioned at the commencement, and only taking on the blue colour at 1000°. The reflexion spectrum of the mixed product shows the presence of both Nd_2O_3,H_2O and Nd_2O_3 until it has been heated at 1000°. J. F. S.

Derivatives of Perceric Oxide. I. C. C. Meloche (*J. Amer. Chem. Soc.*, 1915, **37**, 2338—2346).—Perceric potassium carbonate has been prepared by treating saturated potassium carbonate solution with hydrogen peroxide, adding cerous ammonium nitrate, and heating the mixture at 60° as long as the colour deepens. Carbon dioxide is then passed through the solution until potassium hydrogen carbonate ceases to be precipitated; the solution is cooled to 0°, and the passage of carbon dioxide continued. The mixture is filtered through glass-wool, and left at 5° for forty-eight hours for the perceric potassium carbonate to crystallise. The compound thus obtained is represented by the formula $Ce_2O_4(CO_3)_2,4K_2CO_3,12H_2O$. Job (A., 1899, ii, 486) has described a compound,

$$Ce_2O_3(CO_3)_3,4K_2CO_3,12H_2O,$$

and Baur (A., 1902, ii, 398) a compound,

$$Ce_2O_4(CO_3)_2,4K_2CO_3,10H_2O.$$

It is shown that two-thirds of the available oxygen in the new compound is to be regarded as peroxide oxygen. E. G.

Cerium Compounds. I. Basic Ceric Sulphates and the Colour of Cerium Dioxide. JAMES FREDERICK SPENCER (T., 1915, **107**, 1265—1273).—The hydrolysis of cerium sulphate has been systematically examined on the basis of the phase rule. It is shown that the compound $CeO_2,SO_3,2H_2O$ is the only basic sulphate of cerium which is stable in contact with dilute sulphuric acid (0·370*N*—0·02*N*) at 25°. This compound is a pale yellow, amorphous powder, which is very slightly soluble in water with further hydrolysis. When ceric sulphate is heated at 155—240°, a pure, white basic sulphate, $3CeO_2,4SO_3$, is formed. This compound appears to exist in two modifications, which are both hydrolysed by water, but yield differently coloured, insoluble residues. When cerium dioxide is prepared by heating ceric sulphate at low temperatures, that is, below a red heat, it is pure white in colour, but on prolonged ignition at higher temperatures it shrinks in volume, and becomes pale yellow in colour. This is taken to indicate that the yellow cerium dioxide is a polymeric form of the white variety.

J. F. S.

Electrical Oxidation of Manganous Salts and Some Compounds Obtained Thereby. MATHIAS SEM (*Zeitsch. Elektrochem.*, 1915, **21**, 426—437).—A number of manganous salts have been electrolytically oxidised and the products studied, and in some cases isolated in the solid form. Solutions of manganous sulphate in sulphuric acid are oxidised according to the scheme:

$$MnSO_4 \longrightarrow Mn_2(SO_4)_3 \longrightarrow Mn(SO_4)_2 \longrightarrow [Mn_2(SO_4)_7] \longrightarrow HMnO_4,$$

the whole of the products except the heptasulphate having been isolated. By electrolysing manganous sulphate in dilute sulphuric acid with a double anode, one plate of which was manganese and the other platinum, solutions of manganese disulphate containing 92 grams in 100 c.c. were obtained, a fact which indicates that the descriptions of manganese disulphate which occur in the literature refer to basic derivatives of the disulphate. The electrical oxidation of manganous chloride at 10° only proceeds to the stage manganic chloride, and at 60° there is no indication of the formation of the tetrachloride. The oxidation of manganous acetate in acetic acid solution proceeds to the stage manganic acetate, and this compound separates in large quantities in the pure condition. The most efficient working details for the preparation of this substance are given in the paper. The electrolysis of manganous nitrate in fuming nitric acid leads to the formation of manganic nitrate. This compound could not be isolated either in the free condition or as its double potassium salt. It is also shown that this compound may be formed in the Volhard manganese reaction. The question of the tervalency of manganese is considered, and it is shown that, in addition to tervalent derivatives, there are also double bivalent and quadrivalent derivatives, and that at all temperatures the following equilibrium exists in solution:

$$2Mn''' \quad Mn'' + Mn'''' \rightleftarrows Mn'''Mn''''.$$

This would explain the behaviour of manganic salts on hydrolysis, and also the behaviour of manganese oxides toward dilute acids.

J. F. S.

The Nature of the A2 Transformation in Iron. Kôtarô Honda (*J. Iron Steel Inst.*, 1915, **91**, 199—254. Compare A., 1913, ii, 222, 966; 1914, ii, 526).—The development of heat associated with the A2 transformation is small compared with that at A3. The temperature at which it begins on cooling or ends on heating is nearly constant for steels of different carbon content.

The course of the magnetisation-temperature curves varies with the strength of the magnetising field. Numerous experiments are given to show that the A2 transformation is not allotropic, like A3, but an intermolecular change within the α-phase. The development of heat should take place continuously between low temperatures and the transformation point, continuing parallel with the change of magnetic properties.

C. H. D.

The Diffusion of Carbon in Iron. F. W. Adams (*J. Iron Steel Inst.*, 1915, **91**, 255—270).—Iron and steel lose weight when heated in a vacuum between 900° and 1000°. Clean surfaces will weld together at that temperature, and carbon diffuses from one mass to the other if the initial carbon contents are unequal. Diffusion in such cases is more rapid than cementation by a gaseous agent such as carbon monoxide.

C. H. D.

Iron, Carbon, and Phosphorus. J. E. Stead (*J. Iron Steel Inst.*, 1915, **91**, 140—198. Compare A., 1914, ii, 371).—In alloys containing much carbon, all the phosphorus is concentrated in the portion which is last to solidify. In ordinary slow cooling, a part of the phosphorus remains in solid solution, but the meteoric iron from Bolsom de Mapimi, Mexico, although containing only 0·277% of phosphorus, contains 0·210% in the form of rhabdite, Fe_3P. On re-melting and cooling, this remains completely dissolved, so that very long annealing would be necessary to cause the crystallisation of rhabdite.

When an alloy containing 2% of phosphorus and 0·12% of carbon is submitted to cementation, the carbon dissolves and expels the phosphide from solid solution, forming a liquid. On cooling, a ternary eutectoid of ferrite, cementite, and phosphide is found, closely resembling ordinary pearlite. On heating this alloy in an oxidising mixture to remove carbon, the phosphide, instead of being reabsorbed, is still more completely expelled, forming coarsely crystalline plates.

The white masses of ferrite, rich in phosphorus, known as "ghost lines" in steel, are the last to be invaded by carbon during heating, and the first to part with carbon on cooling. The diffusion of phosphorus in steel is very slow, and the presence of phosphorus retards the diffusion of carbon. Steels containing large proportions of phosphorus therefore require a higher temperature for refining than purer steels.

For detecting the distribution of phosphorus in steel, a reagent is recommended composed of 10 grams of cupric chloride and 40 grams of magnesium chloride, dissolved in the least possible quantity of water, mixed with 20 c.c. of hydrochloric acid, and made up to a litre with alcohol. This is applied in a thin layer to the surface of the specimen, which is then washed with hot water, and finally with alcohol. Those portions of the ferrite which contain least phosphorus become first coated with copper, and the structure is revealed very clearly. C. H. D.

Iron, Silicon, and Carbon Alloys. GEORGES CHARPY and ANDRÉ CORNU-THENARD (*J. Iron Steel Inst.*, 1915, **91**, 276–305).—Thermal and dilatometric experiments show that the A3 temperature rises slightly with increasing silicon, the intensity of the thermal effect at the same time diminishing rapidly. The temperature of the A1 change also rises, but the intensity rapidly decreases, and in annealed specimens soon disappears, owing to the decomposition of carbide by liberation of graphite. The A2 temperature falls, but its intensity does not diminish to the same extent, remaining clearly perceptible even when 7% of silicon is present. It does not appear on the dilatation curves.

The influence of silicon in diminishing the solubility of carbon in iron is shown quantitatively. In some cases the precipitation of graphite may even give rise to a measurable development of heat. C. H. D.

The Heterogeneity of Steels. HENRY LE CHATELIER and JULES LEMOINE (*Compt. rend.*, 1915, **161**, 373—378).—The authors have examined the action of Stead's reagent for studying the distribution of phosphorus in steels (see above) on a number of steels. They find that the success of the reagent depends very largely on the relative proportions of water and alcohol present, and give the following as the most satisfactory composition: methyl alcohol, 100 c.c.; water, 18 c.c.; concentrated hydrochloric acid, 2 c.c.; crystalline copper chloride, 1 gram; crystalline magnesium chloride, 4 grams. Using this reagent on a sample of soft sheet iron, containing manganese 0·50%, phosphorus 0·16%, they obtained very sharp bands, about 0·1 mm. in width, over the whole of the surface of the specimen. The same phenomena were observed with a slightly harder rail steel. Tempering does not modify the position of the bands, but renders their internal structure more homogeneous. The formation of these bands is not due exclusively to phosphorus. They can be produced, in the absence of phosphorus, by the presence of all other substances soluble in ferrite and incapable of diffusion. In fact, almost all steels, even those of good quality, exhibit this striated structure to differing extents, according to the work they have undergone. W. G.

Can the Dissociation Theory be Applied to Solid Solutions in Steels? EDWARD D. CAMPBELL (*J. Amer. Chem. Soc.*, 1915, **37**, 2039—2046).—Experiments are described which show the influence

of heat treatment on the specific resistance of steel and on the colour of the dinitro-derivatives, due to carbides, obtained by dissolving a sample of the steel in nitric acid. The results indicate that there is a close relationship between the concentration of the carbides in solid solution and the specific resistance.

In discussing the application of the dissociation theory to solutions in steels, it is pointed out that, as the solvent is a metal, it would be impossible for the products of ionic dissociation to retain electric charges, and these products are therefore termed "ionoids." The electrolytic activity of ionoids would manifest itself in a manner directly the reverse of that manifested by ions, on account of the opposite nature of the electrical properties of the solvents. Although the ionoids, like ions, tend to acquire energy in the form of electric charges, this energy cannot be retained, on account of the nature of the solvent, and is therefore transformed and dissipated in the form of heat. It is considered that the dissociation theory of solution is just as applicable to solid solutions in metals as to aqueous solutions, but the phenomena when the two solutions were subjected to a difference of potential at two points would reveal themselves in opposite directions. The differences exhibited by the two classes of solutions are not due to any fundamental difference in the atomic relations existing between solutes and solvent, but to the differences in the electrical properties of the solvents. E. G.

The Detection of Burning in Steel. J. E. Stead (*J. Iron Steel Inst.*, 1915, **91**, 398—408).—"Burning" or heating to incipient fusion, favours the diffusion of phosphorus. The first portions to melt are rich in phosphorus. Etching with the cupric reagent (this vol., ii, 779) reveals the parts which have been melted, although etching with picric acid may not show much change of structure. C. H. D.

The Corrosion of Iron in Aqueous Solutions of Inorganic Salts. J. Newton Friend and Peter C. Barnet (*J. Iron Steel Inst.*, 1915, **91**, 336—352).—The loss of weight of electrolytic iron foil immersed in solutions of various salts has been determined, and curves are given to show the influence of concentration and temperature. C. H. D.

The Removal of Rust by Means of Chemical Reagents. J. Newton Friend and C. W. Marshall (*J. Iron Steel Inst.*, 1915, **91**, 357—364).—Sodium citrate has often been used to remove rust from iron. Actually, iron is also dissolved, but a 20% solution leaves a very clean surface. Saturated solutions of boric acid act very rapidly, and only dissolve iron very slowly after the rust has been removed. C. H. D.

Oxidation and Reduction without the Addition of Acid. I. Reaction between Ferrous Sulphate and Potassium Dichromate. Marks Neidle and Joshua C. Witt (*J. Amer. Chem. Soc.*, 1915, **37**, 2360—2368).—A study has been made of the titration

of a ferrous salt with potassium dichromate in the absence of acid, potassium ferricyanide being used as the indicator. The amount of dichromate required to complete the reaction increases with the dilution of the ferrous salt solution. When dry ferrous sulphate is titrated, the result approaches the theoretical. In order to measure the velocity of the reaction, the reaction was stopped by adding ammonia solution, the mixture was filtered, and the dichromate in the filtrate estimated.

The results show that the stoïcheiometric relations in the reaction between potassium dichromate and ferrous sulphate are the same in the presence or absence of acid. In the absence of acid the reaction is instantaneous, except in very dilute solutions. The reaction may be expressed by the equation:

$$3K_2Cr_2O_7 + 18FeSO_4 + (x+6y)H_2O = 3K_2SO_4 + Cr_2O_3,xH_2O + 2Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 6(Fe_2O_3,yH_2O).$$

The colloidal chromic and ferric oxides are precipitated by the sulphate ion in the solution, and adsorb a large quantity of ferric sulphate and smaller quantities of the other two sulphates. E. G.

Electrodeposition of Nickel. C. W. Bennett, C. C. Rose, and L. G. Tinkler (*J. Physical Chem.*, 1915, **19**, 564—568).—Experiments have been carried out on the electrodeposition of nickel from acid and alkaline solutions, using both stationary and rotating electrodes. It is shown that with nickel ammonium sulphate solutions the efficiency of deposition on a rotatory cathode, as well as on a stationary one, may be changed by changing the concentration of the hydrogen ions. If the solution is maintained just sufficiently alkaline, a high efficiency of deposition is attained, and this efficiency is maintained for long periods when the cathode is rotated. When the concentration of hydrogen ions is practically zero, as in the case of a strongly alkaline solution, nickel is deposited more easily than the other ions, but with low efficiency. The low efficiency is occasioned by the impoverishment of the solution in nickel ions. Rotation of the cathode prevents this impoverishment, and therefore tends to increase the efficiency, whereas in the cases of solutions where hydrogen ions are present the rotation of the cathode tends to prevent impoverishment of the hydrogen ions, and consequently decreases the efficiency of nickel deposition. With a solution of 5% nickel cyanide and 7% potassium cyanide, using a current density of 5 amperes per square decimetre, a maximum efficiency of 0·057% was obtained with stationary electrodes, but on rotating the cathode the efficiency increased, the value 0·13% being obtained with a revolution number of 500, and 1·65% with a revolution number of 1000. J. F. S.

Hydrated Chromic Oxide. II. C. F. Nagel, jun. (*J. Physical Chem.*, 1915, **19**, 569—570).—Fischer and Herz consider that hydrated chromic oxide is peptonised, and not dissolved, by alkali hydroxide (A., 1902, ii, 564). A number of experiments have been carried out to study this point further. Freshly precipitated chromic hydroxide was treated with an excess of potassium hydr-

oxide, and the solution kept in a glass-stoppered bottle. After about three weeks a considerable amount of the chromium hydroxide had been deposited, and in two months the major portion had been deposited, leaving only a faintly coloured solution. A similar solution was passed through a collodion filter, when a colourless solution came through, leaving the chromium hydroxide behind. When chromium hydroxide is heated with a solution of chromic chloride, some of the hydroxide passes into solution, forming what has hitherto been regarded as a basic chloride. When such a solution is run through a collodion filter the whole of the hydroxide remains behind, and non-basic chromic chloride passes through. Hence chromic chloride solution merely peptonises chromic hydroxide, and there is no evidence of the formation of a basic salt. Peptonised chromic hydroxide cannot be extracted from solution with benzene or light petroleum, but goes into the dineric interface. J. F. S.

Atomic Weight of Molybdenum. JOHN H. MÜLLER (*J. Amer. Chem. Soc.*, 1915, **37**, 2046—2054).—An account is given of experiments to determine the atomic weight of molybdenum by the conversion of the pure metal into the trioxide. The molybdenum was prepared by the reduction of the trioxide. The purification of the trioxide was effected by subliming it in quartz vessels, and subsequently carrying out a fractional sublimation in hydrogen chloride in order to ensure the absence of tungsten. The sublimed hydroxychloride was dissolved in water, treated with dilute ammonia, and evaporated to dryness in a platinum dish. The residue was ignited in a quartz vessel. The oxide was placed in a quartz boat, and heated in a quartz tube in a current of pure, dry hydrogen. It was found that quartz apparatus is not affected by molybdenum or its oxides, and that the metal thus prepared does not contain any absorbed hydrogen.

Weighed quantities of the pure molybdenum were oxidised by heating them in quartz boats, first in a current of air, and subsequently in oxygen, special precautions being taken to avoid loss of the oxide by volatilisation. The average results of eight experiments with three different samples of molybdenum gave an atomic weight of 96·029.

Molybdenum has D_4^{26} 10·281, and molybdenum trioxide D_4^{26} 4·696.

E. G.

Molybdic Acid Recovery. C. G. ARMSTRONG (*J. Ind. Eng. Chem.*, 1915, **7**, 764).—The waste molybdic acid residues obtained in steel analysis are filtered and evaporated, fresh quantities being added until a considerable amount of precipitated molybdic acid is obtained; sufficient liquid must be left to keep the iron in solution. After cooling, the precipitate is washed with cold water, then treated with an excess of ammonia, the mixture heated, filtered, and a quantity of molybdic acid is added sufficient to bring the molybdic acid content up to 0·2825 gram per c.c.; the solution is now mixed with the requisite amounts of nitric acid and water to constitute the usual molybdic acid reagent. W. P. S.

Group of Bismuth Tellurides. M. AMADORI (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 200—205).—The system Bi_2Te_3–Bi_2S_3 has been subjected to thermal and micrographic investigation. The results indicate the formation of the compound, Bi_2Te_3,Bi_2S_3, which solidifies at 615°, and forms (1) with Bi_2Te_3, a eutectic mixture containing about 3 mol. % of Bi_2S_3 and solidifying at 570°, and (2) with Bi_2S_3, a eutectic mixture with a composition and solidification point approximating to those of the compound, Bi_2Te_3,Bi_2S_3. No isomorphism is observable between Bi_2Te_3 and Bi_2S_3 or between the above compound and its components. In the experimental conditions employed, no evidence is obtainable of the formation of either the compound, $2Bi_2Te_3,Bi_2S_3$, or mixed crystals of the type of the natural tetradymites. The micrographic results are in accord with those obtained thermally. T. H. P.

Transformations in Alloys of Gold and Copper. N. KURNAKOV, S. SHEMTSCHUSHNI, and M. ZASEDATELEV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 871—897).—That alloys of copper and gold represent a typical example of isomorphous mixtures of two metals in all proportions has been shown by investigations of their fusion diagrams (A., 1907, ii, 525), microstructure, electrical conductivity (compare Mathiessen, *Ann. Phys. Chem.*, 1861, **100**, 190), hardness (A., 1908, ii, 932), and other properties. The original measurements of the hardness (*loc. cit.*) were made on cast specimens by means of the sclerometer. Later, after Brinel's method had been found to yield good results in other cases, it was applied to copper–gold alloys. The preliminary measurements confirmed the existence of a very distinct maximum of hardness (200 kilograms per sq. mm.) at about 50 at. % of gold, but yielded a diagram, the form of which was not in agreement with that required by theory for a series of solid solutions. The authors have, therefore, carried out a new series of systematic investigations of the cooling curves, microstructures, hardness, and electrical conductivities of the cooled and tempered alloys. The results of these measurements, which are given in detail, show that the continuous isomorphous mixtures of copper and gold, or the α-solutions, are stable only at temperatures of 367·3° (50 at. % Au) and 370·8° (25 at. % Au). Below these transformation points, decomposition of the isomorphous mixtures occurs, with separation of the definite compounds, CuAu and Cu_3Au, which form solid solutions with excess of their components. The very simple forms of electrical conductivity and hardness diagrams previously observed correspond with a continuous series of α-solid solutions of gold and copper, the decomposition of these not being noticed during the cooling of the fused alloy. The transformation of such a solution with separation of the new phases requires a moderately long time, and the necessary tempering may be considerably delayed.

Closer examination of the influence of tempering and cooling on the alloy containing 50 at. % Au reveals an interesting difference in properties between the α-solid solution and the auride, CuAu, which is the product of the transformation at temperatures below

370·8°. The α-solution is a comparatively soft, plastic substance, which can be rolled or drawn out into wire, whilst the compound, CuAu, exhibits marked hardness and brittleness, in consequence of which rolling or drawing is impossible. Thus, with this alloy (50 at. % Au), the influence of tempering and cooling on the properties of the solid is the reverse of that with many other metals.

T. H. P.

New Method of Preparing Chloro- and Bromo-triammino-platinous Haloids. (Cleve's Salts.) LEO ALEXANDROVITSCH TSCHUGAEV (T., 1915, **107**, 1247—1250).—The methods hitherto used for the preparation of the chloride $[ClPt(NH_3)_3]Cl$ have depended either on the addition of ammonia to dichlorodiamminoplatinum, $[Cl_2Pt(NH_3)_2]$, or on the elimination of ammonia from tetra-amminoplatinous chloride, $[Pt(NH_3)_4]Cl_2$. These methods suffer from the defect that the union or elimination of ammonia cannot be stopped at the stage required. The following is an improved method, the difficulties of the addition of ammonia being overcome by using a compound, namely, potassium cyanate, which evolves ammonia gradually when hydrolysed.

One gram of *cis*dichlorodiamminoplatinum (Peyrone's chloride) is boiled with 0·7 gram of potassium cyanate and 18—20 c.c. of water, shaking meanwhile. After solution is complete, the boiling is continued for one minute. Several portions prepared in this way are combined, and heated with an excess of hydrochloric acid, D 1·19 (4 c.c. for each portion), the whole heated to boiling, and then cooled. After collecting the unchanged dichlorodiammino-platinum which separates, an excess of potassium platinochloride is added to the filtrate, whereby a precipitate is obtained consisting of a mixture of tetra-amminoplatinous platinochloride and of chlorotriamminoplatinous platinochloride (Cleve's salt),

$$[ClPt(NH_3)_3]_2PtCl_4.$$

This mixture is then separated by taking advantage of the fact that the latter compound is fairly readily soluble in hot water. The yield of platinochloride thus obtained is about 50% of the theoretical, calculated on the part of the dichlorodiamminoplatinum which enters into reaction. The chloride is obtained from the platino-chloride by the method described by Cleve and Klason (A., 1903, i, 224).

Using a similar procedure to that given above, and replacing the chloro- by bromo-compounds, *bromotriammino-platinous platino-bromide*, $[BrPt(NH_3)_3]_2PtBr_4,H_2O$, is obtained in the form of violet plates.

T. S. P.

Mineralogical Chemistry.

Composition of Coal. III. David Trevor Jones and Richard Vernon Wheeler (T., 1915, **107**, 1318—1324. Compare T., 1914, **105**, 241, 2562).—A continuation of previous work. Finely-powdered bituminous coal was extracted in a Soxhlet apparatus with pyridine. The extract (*a*) was then extracted with chloroform,

a portion (*c*) was soluble in chloroform, and a residue (*b*) remained undissolved. The three dried extracts were then distilled separately in a vacuum. The distillate was collected successively in an air-cooled receiver and in a receiver cooled by solid carbon dioxide and ether, whilst the uncondensed gases were collected separately. The residue (*a*) evolved gases at 200°; at 390° heavy vapours were given off, and the distillation was completed at 450°. The distillate in the air-cooled receiver consisted of phenols, and a little acid water; the distillate in the second receiver consisted of 0·5 c.c. of oil, which contained 86·44% carbon and 11·35% hydrogen. The residue in the distilling flask was unchanged in appearance, and consisted of a finely divided brown powder. The residue (*b*) evolved gases at 180—200° and oils at 390°, and the distillation was complete at 450°. The air-cooled receiver contained acidic water and oils, 40% of which were phenols and the residue of a resinous nature. The residue in the flask was a fine powder, which exhibited no tendency to cake. The residue (*c*) when distilled softened at 90° and melted at 102°, gases being evolved at 170°; liquids distilled over at 180°, and these contained in addition to pyridine and chloroform an oil containing 86·5% carbon and 9·88% hydrogen. This oil distilled unchanged at 255° under atmospheric pressure, and was not hydroxylic in character. On distilling (*c*) further, paraffin wax and resinous matter came over at 250°, and large volumes of gases were evolved at 320°, whilst the contents of the distilling flask swelled up and caked at 400°. The formation of the pitch in case (*c*) shows that the caking properties of coal are due to the resinous matter. The gases evolved below 300° consisted in each case almost entirely of carbon monoxide and carbon dioxide in the ratio 1 : 3. The gases evolved between 300° and 450° were as follows: (*a*) 0·4% olefines, 3·7% carbon dioxide, 5·1% ethylene, 13·6% carbon monoxide, 14·8% hydrogen, and 62·4% paraffins; (*b*) 0·2% olefines, 4·4% carbon dioxide, 5·2% ethylene, 12·1% carbon monoxide, 19·1% hydrogen, and 59·0% paraffins; (*c*) 0·1% olefines, 2·0% carbon dioxide, 1·9% ethylene, 8·4% carbon monoxide, and 87·6% paraffins. The work shows that the main bulk of the liquid distillate of coal arises from the resinous substances, but a small, distinctive portion is due to the "humic substances." The "humic substances" yield mainly phenols, whereas the resinous substances yield no phenols, but paraffins, olefines, and naphthalenes. J. F. S.

Phosphorite of the Isle of Ajawi. A. Wichmann (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 214—220).—A description of the appearance, occurrence, and probable origin of a phosphorite found in the island of Ajawi. It is of a yellow to reddish-brown colour, D 2·78, and hardness = 6. Under the microscope it presents the appearance of a structureless mass, intersected by irregular fissures. Thin sections show dark spots, apparently of organic origin. The available analyses of the mineral are insufficient for the deduction of a satisfactory formula. It is considered probable that the phosphorite rocks of Ajawi represent the ruins of an atoll in which

the excrements of birds producing guano collected, whereby phosphorite was produced by the action of the phosphoric acid on the coral-limestone. H. M. D.

Childrenite from Crinnis Mine, Cornwall, and Eosphorite from Poland, Maine. JULIEN DRUGMAN (*Min. Mag.*, 1915, **17**, 193—201).—Analysis I is of minute crystals of childrenite occurring in crevices in slate from the Crinnis mine, near St. Austell. The crystals are pale buff to almost colourless, but are usually coated with a brown layer of hydrated ferric oxide. The results agree with Penfield's formula, $2(Fe,Mn)(OH)_2,Al_2O_3,P_2O_5,2H_2O$. The material contains a little more iron and correspondingly less manganese than the chlidrenite from the George and Charlotte mine near Tavistock:

	P_2O_5.	Al_2O_3.	FeO.	MnO.	CaO.	Na_2O.	H_2O.	Insol.	Total.
I.	29·80	21·20	28·30	3·35	0·90	0·25	15·30	0·95	100·05
II.	31·01	22·23	5·14	26·02	0·81	—	15·27	—	100·48

Eosphorite as small, roughly radiated aggregates of prismatic crystals of a pale pink colour occurs with rhodochrosite at Poland, Maine. The mean of three partial analyses is given under II, agreeing with the above formula, with manganese predominating over iron. This material contains rather less iron that the original eosphorite from Branchville, Connecticut. Measurements and optical determinations are given of the orthorhombic crystals, $a:b:c=0·7724:1:0·5126$. L. J. S.

Bassetite and Uranospathite, New Species of the Autunite Group. A. F. HALLIMOND (*Min. Mag.*, 1915, **17**, 221—236).—The material from Cornwall hitherto regarded as autunite is shown to be distinct from the original autunite from Autun, in France, and to belong to two new species, for which the names bassetite and uranospathite are proposed. Both form yellow, platy crystals with a micaceous cleavage, and in general characters they resemble the other "uranium-micas." Bassetite is monoclinic ($a:b:c=0·3473:1:0·3456$; $\beta=89°17'$), D 3·10, and is probably the material analysed by Church (T., 1875, **28**, 109), which gave the formula $Ca(UO_2)_2(PO_4)_2,xH_2O$, where x is probably 8. Uranospathite is orthorhombic and pseudo-tetragonal; the density (D 2·50) and refractive indices (β 1·510) are low. The behaviour of the mineral when heated, and its absorption-spectrum, suggest that it is a hydrated uranyl salt. L. J. S.

Albite from Alp Rischuna, Switzerland. W. J. LEWIS (*Min. Mag.*, 1915, **17**, 178—188).—A detailed crystallographic description is given; $a:b:c=0·6335:1:0·5564$; $\alpha=93°58'$, $\beta=116°21'$, $\gamma=87°31\frac{1}{4}'$. Analysis by H. B. Cronshaw gave:

SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	Ign.	Total.
68·28	19·95	0·45	11·35	0·06	0·10	100·19

L. J. S.

Garnet from the English Lake District. J. Frederick N. Green (*Min. Mag.*, 1915, **17**, 207—217).—Crystals of almandine are of sporadic distribution in the volcanic rocks of the Lake District. They are associated with iron pyrites, and have probably been formed by circulating solutions under high hydrostatic pressure during the solfataric stage of the volcanic episode. Analysis by G. T. Holloway of crystals from andesite in Riggindale gave:

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	Alkalis, etc.	Total
35·90	1·53	20·20	6·12	27·48	3·84	1·42	3·28	[0·23]	100·00

L. J. S.

Analytical Chemistry.

A Simple Method of Converting the Duboscq Colorimeter with a Nephelometer. W. R. Bloor (*J. Biol. Chem.*, 1915, **22**, 145—149).—The Richards nephelometer, and the converted Duboscq colorimeter of Kober have disadvantages. These are overcome by the modifications which are here described with figures and other details. W. D. H.

Automatic Zero Burette. A. T. Mertes (*J. Ind. Eng. Chem.*, 1915, **7**, 786—787).—A side-tube at the bottom of the burette is attached by means of a length of rubber tubing to a glass tube extending to the bottom of a reservoir containing the solution; a pinch-clamp is provided on the rubber tubing. A short glass tube carrying a side-tube fits into the top of the burette, and the latter is filled by suction, a length of rubber tubing being fitted on the side-tube for this purpose. A narrow glass tube passes down the tube at the top of the burette, and the lower end of this narrow tube is level with the zero point; the part of the narrow tube above the burette is bent downwards, and connects with a tube fused into the side of the reservoir tube and passing down inside the latter to the bottom of the reservoir. Any excess of solution drawn into the burette is siphoned off through the narrow tube, and returns to the reservoir. W. P. S.

Methylene-blue and its Use in Analytical Chemistry. F. W. Atack (*J. Soc. Dyers*, 1915, **31**, 183—188; 203—208).—Methylene-blue and leucomethylene-blue are capable of wide application in analysis; their acid solutions are very stable, and methylene-blue is converted quantitatively into its leuco-compound by reducing substances, the leuco-compound being equally readily oxidised by oxidising substances. Methylene-blue hydrochloride yields characteristic precipitates with normal salts of certain inorganic acids (perchlorate, periodate, permanganate, dichromate, persulphate,

etc.); it is reduced by all the lower sulphur acids, by hydrazine hydrate, phenylhydrazine, and alkaline pyrogallol, but not quantitatively, whilst it is not affected by nitrites, hypophosphites, and arsenites. Leucomethylene-blue, prepared by reducing methylene-blue with phenylhydrazine, is oxidised by chlorates, but not by perchlorates; nitrites and nitroso-compounds oxidise leucomethylene-blue rapidly. Methylene-blue solution for quantitative work is standardised against titanous chloride solution. Oxidising substances, such as nitrites, dissolved oxygen in water, nitroso-compounds, quinones, azo-compounds, etc., may be estimated by means of leucomethylene-blue solution. Potassium is estimated by precipitating it as potassium sodium cobaltinitrite, and treating the latter in alkaline solution with leucomethylene-blue solution, the methylene-blue formed being then titrated with titanous chloride solution. 1:2-Diketones may be estimated by reduction with an excess of titanous chloride solution, and titrating the excess of the latter with methylene-blue solution; certain oximes are estimated in a similar way. W. P. S.

A Simple Method for the Detection and Estimation of Metalloids in Organic Compounds. JOHN. A. MANDEL and CARL NEUBERG (*Biochem. Zeitsch.*, 1915, **71**, 196—213).—Organic compounds can be oxidised by 15% hydrogen peroxide in the presence of iron salts in such a way that the metalloid is set free from combination. The reaction takes place very rapidly on warming, and is useful when employed for qualitative analysis. Compounds which are insoluble in water or dilute acids can be oxidised in glacial acetic acid. The reaction can also be used often for quantitative estimation, but not in all cases. When the method is applicable, it offers a rapid means for quantitative estimation of phosphorus, arsenic, the halogens, and sulphur. The process is illustrated by numerous examples. When the substance under investigation is volatile, the oxidation is carried out in a vessel fitted with a reflux condenser. Substances insoluble in water or acids can be oxidised in alkaline (preferably ammoniacal) solution; when insoluble in water or aqueous solutions of acids or alkalis, they can be oxidised in glacial acetic acid. In some cases the substances are heated with sulphuric acid until charring takes place, and the oxidation is completed by hydrogen peroxide in the presence of an iron salt. In estimating the halogens, the oxidation is carried out in the presence of silver nitrate. Phosphorus and sulphur can be estimated in the same sample. S. B. S.

Estimation of Hydrogen in Mixtures of Gases by Catalytic Absorption. E. BOSSHARD and E. FISCHLI (*Zeitsch. angew. Chem.*, 1915, **28**, 365—366).—A mixture of sodium oleate and metallic nickel is used to absorb the hydrogen; the nickel is prepared by reducing nickel oxide in hydrogen at 340°. The mixed gas should be freed previously from carbon dioxide, heavy hydrocarbons, oxygen (by ammoniacal cuprous chloride solution, and not by phosphorus), and carbon monoxide; the residual gas is then passed

into an absorption pipette containing concentrated sodium oleate solution mixed with 3% of its weight of reduced nickel, shaken for three minutes, then passed into a second pipette containing a similar mixture, again shaken for three minutes, and, after the addition of 1 c.c. of alcohol to break down the foam, the residual gas is passed back into the measuring burette. The hydrogen is removed completely by this treatment, whilst any nitrogen and methane which may be present are not absorbed. The results obtained agree well with those obtained by the ordinary explosion method. W. P. S.

Method of Collecting and Analysing Industrial Gases. II. Gasometer-aspirator with Uniform Velocity. ARMAND GAUTIER (*Bull. Soc. Chim.*, 1915, [iv], **17**, 297—301).—The aspirator consists essentially of a large, tin-lined steel cylinder of more than 100 litres capacity, which does not undergo deformation when evacuated. It is connected to the source of gas to be examined through a regulator, constructed as follows. A narrow steel tube 1 metre in length, having a narrow slit extending for 76 cm. from its bottom end, and a needle valve at its top end, is sealed into a stout glass tube having a side tubulure, and its base dipping into mercury. The aspirator and the regulator are evacuated, and thus the slit in the steel tube is almost closed. As the gas enters and the pressure in the apparatus gradually rises, the mercury slowly falls in the glass tube, a longer length of the slit in the steel tube being consequently exposed, and this maintains the flow of the gas at a uniform velocity. Both the glass and the steel tubes are graduated so that the pressures can be read off. The regulator is figured in the original. W. G.

Method of Collecting and Analysing Industrial Gases. III. Mixtures of Air, CO, CO_2, SO_2, H_2O, H_2, C_2H_2, C_2H_4, CH_4, etc. ARMAND GAUTIER (*Bull. Soc. Chim.*, 1915, [iv], **17**, 301—306).—The gases to be analysed are aspirated by means of the aspirator already described (preceding abstract), and if flue gases, are collected and filtered by means of the apparatus previously described (compare this vol., ii, 699). Prior to entering the gasometer aspirator (*loc. cit.*), the gases are passed through weighed absorption tubes containing: (1) pumice and sulphuric acid to absorb water vapour; (2) potassium hydroxide to absorb carbon dioxide and sulphur dioxide; (3) a concentrated solution of sodium hyposulphite, followed by a tube containing potassium hydroxide to absorb oxygen. Any hydrogen sulphide or hydrogen chloride will be absorbed in tube (2). These gases can be regenerated and estimated separately by the usual methods. The remaining gases are collected in the gasometer, and, after being measured, a portion of the mixture is pumped off and analysed, as follows. It is first passed through a tube containing pumice moistened with sulphuric acid to absorb any trace of moisture, and then through a weighed spiral absorber (compare A., 1900, ii, 366) filled with a saturated solution of iodine bromide in acetic acid, where all the unsaturated

hydrocarbons are absorbed, a small absorption tube containing potassium mercuri-iodide, and having a tube of potassium hydroxide attached, being connected to this to absorb any iodine bromide and acetic acid passing over. The gases next pass through a U-tube filled with iodine pentoxide heated at 80—100°, and then over a column of reduced copper to a weighed absorption tube filled with concentrated potassium hydroxide, the carbon monoxide being thus estimated. The gases finally pass through a combustion tube, 25 cm. long, filled with copper oxide and heated to a red heat, to which is connected the ordinary apparatus for absorbing water vapour and carbon dioxide. The saturated hydrocarbons and free hydrogen are thus estimated. The nitrogen is determined by difference. This method is only accurate to within from 2—10%. W. G.

Electrical Resistance of Subterranean Waters: Dilution Curves. C. Pieri (*Ann. Chim. applicata*, 1915, **4**, 93—111).—The author has traced the curves showing the variation of electrical conductivity with dilution for a soft, a hard, and a mineral water occurring naturally, and also for an artificial solution containing potassium, sodium and calcium chlorides, and magnesium and calcium sulphates. The results obtained show that the characterisation and supervision of a source of underground water are best effected, not by the electrical conductivity of the water, but by the corresponding conductivity-dilution curve. The discontinuity sometimes observable in these curves is probably dependent on hydrolytic changes, and, consequently, on the proportions of carbon dioxide and of alkali and alkaline-earth bases present. T. H. P.

The Employment of Borax and Boric Acid Mixtures for the Colorimetric Measurement of the Hydrion Concentration of Sea-water. Sven Palitzsch (*Biochem. Zeitsch.*, 1915, **70**, 333—343).—Mixtures of $M/20$ borax with $M/5$ boric acid to which sodium chloride to the amount of $M/20$ has been added are convenient for the colorimetric estimation of the hydrion concentration of sea-water. The hydrion concentrations of mixtures containing from 10 c.c. of the borate solution and no boric acid to 0·3 c.c. of borate solution and 9·7 c.c. of boric acid have been measured electrometrically by the author, and the results are tabulated. Methods for controlling the purity of the borax and boric acid are also given. S. B. S.

Anodic Potentials of Silver. II. Their Rôle in the Electrolytic Estimation of the Halogens. John Henry Reedy (*Amer. J. Sci.*, 1915, [iv], **40**, 400—412. Compare this vol., ii, 733).—A number of experiments have been carried out on the electrolysis of alkali haloids by means of silver anodes with the object of studying the conditions under which estimations of the halogens, chlorine, bromine, and iodine, must be effected to obtain trustworthy results. Further experiments were made on the estimation of one halogen

in the presence of the others. It is shown that the success of the process depends on the anodic potential, and this must be carefully controlled by means of a third electrode during the process, and must not exceed the maximum potential characteristic of each separation if a perfect separation is to be achieved. The maximum anode potentials are: for iodine, 0·190 volt; for bromine, 0·400 volt; and for chlorine, 0·505 volt. In no circumstances must the anode potential exceed 0·521 volt, for at this value silver commences to dissolve from the anode. The course of the electrolysis cannot be controlled by regulation of the current strength independently of the anode potential. The main result of the work is, therefore, that chlorine cannot satisfactorily be estimated by an electrolytic process, since its deposition potential and the solution potential of silver are practically identical. The other halogens may be easily estimated in this way, and completely separated from one another and from chlorine, if the anode potential is suitably adjusted and the limits of concentration necessary maintained. J. F. S.

Estimation of Chloride and Bromide in the Presence of Each Other. Arthur Meyer (*Chem. Zeit.*, 1915, **39**, 708).—A portion of the solution containing chlorides and bromides is titrated with $N/10$ silver nitrate solution; in another equal portion of the solution, the chloride and bromide are precipitated by the addition of silver nitrate solution; the precipitate is collected in a Gooch crucible, dried, and weighed. The weight of silver in the mixed haloid precipitate is known from the result of the preliminary titration; on subtracting this amount of silver from the weight of the precipitate, the weight of the chlorine and bromine together is obtained, and the quantities of the two halogens are then found by a simple calculation. W. P. S.

Detection of Iodine in Urine. Losser (*J. Pharm. Chim.*, 1915, [vii], **12**, 229—230; from *Pharmazevtizeski*, 1915, **54**, 265).—A few drops of the urine are mixed thoroughly on a watch-glass with a small quantity of mercurous chloride. If iodine is present, a yellow coloration, due to the formation of mercurous iodide, develops. The test will detect 0·01 gram of iodine per 100 c.c. of urine; the presence of sugar or albumin does not interfere with the reaction. W. P. S.

Estimation of Iodine in the Presence of Organic Matter. Robert B. Krauss (*J. Biol. Chem.*, 1915, **22**, 151—157).—The methods at present in use leave much to be desired. In a solution of iodides, or in animal tissues, the iodine may be directly estimated by the palladous iodide colorimetric method. No iodides, iodates, or halogens, usually the source of errors, are added in this method. W. D. H.

Estimation of Oxygen in Water. II. Jan Smit (*Chem. Weekblad*, 1915, **12**, 819—822).—A criticism of the method recom-

mended by the Dutch *Codex Alimentarius* for estimating oxygen in water. A. J. W.

Apparatus for the Estimation of Dissolved Air in Water. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1915, **28**, 366—368).—The water is collected in a 250 c.c. flask of known capacity containing 5 grams of marble previously washed with hydrochloric acid; if the analysis is not carried out at the place where the sample is taken, precautions must be taken to prevent loss of gases from the flask and entry of air thereto. The dissolved gases are estimated as follows. A small pipette-shaped vessel is filled with 25% hydrochloric acid; the lower stem of this vessel passes through a rubber stopper which fits into the neck of the flask holding the water, and the upper neck, provided with a tap, passes into the bottom of an ordinary small gas-measuring burette surrounded by a vessel containing a mixture of 10% sodium hydroxide solution and 5% potassium sodium tartrate solution. When the rubber stopper is inserted in the neck of the flask and the tap on the stem of the pipette is opened, the hydrochloric acid diffuses into the water, reacts with the marble, and the liberated carbon dioxide, together with the dissolved air, passes up into the gas burette. After about forty-five minutes, all the air will have been expelled from the water and collected in the burette, the carbon dioxide being absorbed by the alkali solution. The total volume of the air is then measured under the usual conditions; the oxygen present may be estimated by absorption in alkaline sodium hyposulphite solution. W. P. S.

A Microaërotonometer. TOYOJIRO KATO (*J. Physiol.*, 1915, **50**, 37—41).—A modification of Barcroft's instrument; the new apparatus is capable of dealing with 0·1 c.c. of blood, and is accurate, and will be found specially useful in clinical work. W. D. H.

Estimation of Sulphurous Acid in Sulphites and Hydrogen Sulphites. EDMUND KNECHT and EVA HIBBERT (*J. Soc. Dyers*, 1915, **31**, 209—210).—The method depends on the reduction of chromate by sulphur dioxide according to the equation:

$$2CrO_3 + 3SO_2 + 3H_2O = Cr_2O_3 + 3H_2SO_4,$$

and subsequent titration of the excess of chromate by titanous chloride solution. The total sulphur dioxide in sodium hydrogen sulphite is estimated by adding a definite volume of a solution of the sample to 20 c.c. of $N/10$-dichromate solution previously rendered alkaline with sodium hydroxide. The mixture is then acidified with sulphuric acid, and the excess of dichromate titrated with standardised titanous chloride solution and iron-alum solution. W. P. S.

Titration of Nitrates with Ferrous Sulphate. FRED C. BOWMAN and W. W. SCOTT (*J. Ind. Eng. Chem.*, 1915, **7**, 766—769). —The nitric acid solution to be titrated should contain from 0·3

to 0·6 gram of HNO_3 (free or combined) per 10 c.c. One hundred c.c. of concentrated sulphuric acid are placed in a beaker, which is set in a porcelain basin filled with cold water, 10 c.c. of the nitric acid solution are added slowly, and the mixture is titrated with ferrous sulphate solution, the end-point being denoted when the colour of the mixture changes from yellow to faint brown or pink. During the titration the temperature should not be allowed to rise above 60°; it is better to keep it below 40°. The ferrous sulphate solution used is prepared by dissolving 176·5 grams of crystallised ferrous sulphate in 400 c.c. of water, adding this solution to 500 c.c. of dilute sulphuric acid (1 : 1), and diluting the mixture to 1 litre. Each c.c. of this solution is equivalent to 0·02 gram of HNO_3, but the solution should be standardised against a known quantity of nitric acid. From the volume of ferrous sulphate solution required for the titration, 0·2 c.c. is deducted in every case, since this is the quantity required to produce the brown tint of the end-point. Nitrites do not interfere with the titration, but chlorates, bromates, iodates, chlorides, bromides, and iodides should not be present. With care, the error does not exceed 1/300 of the amount of the nitric acid estimated.

W. P. S.

Modification of Pelouze's Method for Estimating Nitrates. E. A. Letts and Florence W. Rea (*Proc. Roy. Soc. Edin.*, 1915, **35**, 168—169).—The method described consists in heating a weighed quantity of the specimen containing the nitrate with a measured volume of standard ferrous sulphate containing a little free sulphuric acid, and estimating the amount of ferrous sulphate unchanged by means of standard potassium permanganate. Experimentally the estimation is carried out by placing 10 c.c. of *N*-ferrous sulphate and 5 c.c. of concentrated sulphuric acid in a 200 c.c. flask, and cooling. Then an inverted condenser is attached to the flask and the air expelled by a current of pure carbon dioxide; the condenser is then removed for a moment, and the sample added, and the condenser replaced and the flask heated for about fifteen to thirty minutes. The contents of the flask are then cooled and titrated with standard permanganate solution. The figures given in the paper show that the method is both trustworthy and accurate. It is specially recommended for the estimation of nitrates in water analysis. J. F. S.

Manonitrometer for the Analysis of Nitro-cotton, Nitration Acid, etc. V. Planchon (*Ann. Chim. anal.*, 1915, **20**, 189—197).—An apparatus, termed a manonitrometer, for the estimation of nitrogen in nitrocellulose, consists of a strong glass bottle or flask of about 750 c.c. capacity, closed by a metal stopper carrying a T-piece, the stem of which extends into the neck of the bottle; a rubber ring between the stopper and the top of the neck makes the air-tight joint, the stopper being secured by a screw-clamp passing round the bottle and over the stopper. One branch of the T-piece is provided with a tap, and is connected with a pump,

whilst the other branch is connected with the upper end of a vertical barometer tube; the latter is provided with an adjustable scale and a mercury reservoir. Fifteen c.c. of mercury (204 grams) and 50 c.c. of concentrated sulphuric acid are placed in the bottle, a weighed quantity of about 2·5 grams of nitrocellulose are introduced, and the air is exhausted from the apparatus. The zero-point of the scale is then placed at the level of the mercury in the barometer tube, the tap leading to the pump is closed, and the contents of the bottle are shaken. When nitric oxide ceases to be evolved, as is shown by the mercury level remaining constant, the bottle is immersed in a bath of cold water, and when the temperature is constant, the pressure is read on the barometer scale. The pressure, temperature, capacity of the apparatus, and the weight of substance being known, the percentage quantity of nitrogen present can be calculated. In determining the capacity of the apparatus, a correction must be made for the sum of the volumes of the mercury, sulphuric acid, and nitro-substance in the bottle. The strength of the sulphuric acid employed may vary from 93% to 97% of actual H_2SO_4; prolonged agitation of the reacting mixture does not decrease the volume of the liberated nitric oxide, and the method possesses the advantage that a relatively large quantity of substance may be taken for the estimation. The apparatus may also be used for the estimation of nitrogen in nitration acid, nitrates, etc. W. P. S.

Nephelometric Estimation of Phosphorus. Philip Adolph Kober and Grete Egerer (*J. Amer. Chem. Soc.*, 1915, **37**, 2373—2381).—In connexion with some work on the nucleases (Kober and Graves, A., 1914, ii, 691) a suitable method was needed for the nephelometric estimation of phosphorus. Pouget and Chouchak (A., 1909, ii, 266; 1911, ii, 823) have shown that an insoluble precipitate of strychnine phosphomolybdate is formed when a solution, containing sodium molybdate, strychnine sulphate, and nitric acid, is added to a solution of a phosphate in nitric acid. This reaction has been studied, and found to be neither constant nor quantitative; it was also observed that the reagent gradually becomes yellow. By substituting hydrochloric acid for the nitric acid, however, the reagent is rendered colourless and stable, and capable of giving quantitative results when applied in nephelometry. Experiments have shown that 0·05 mg. of phosphorus in 10 c.c. of solution (or 1 : 2,000,000) can be readily estimated by this method. E. G.

Comparison of the Gravimetric Methods Employed in Analytical Chemistry for Estimating Phosphoric Acid with the Processes Used in Technical Analysis. A. Korevaar (*Chem. Weekblad.*, 1915, **12**, 814—818).—A review of the more important scientific methods and technical processes for the estimation of phosphoric acid. A. J. W.

Factor to be Used for the Calculation of the Phosphoric Acid in Neumann's Method. The Factor as Influenced by the Water Used for Washing the Yellow Precipitate. S. L. Jodidi and E. H. Kellogg (*J. Franklin Inst.*, 1915, **180**, 349—367).—Jodidi (this vol., ii, 577) has confirmed the view that in Neumann's method of estimating phosphorus the theoretical factor, 0·554, is too low, and should be replaced by the factor 0·57. The present work was undertaken in order to elucidate the causes of this discrepancy.

It has been found that the factor rises to some extent as the amount of water used for washing the ammonium phosphomolybdate precipitate is increased, and that the precipitate is not entirely insoluble in the liquid in which it is produced. The larger the amount of the phosphorus-containing compound used for the analysis, the smaller is the percentage of phosphorus lost in the filtrate and washings. Instead of washing the precipitate three or four times with 150 c.c. of water as recommended by Neumann, it is sufficient to wash it three times with 50 c.c. of water. It is also found that a 300 c.c. round-bottomed flask is more convenient for the formation of the precipitate than the 750 c.c. flask commonly employed for the purpose. The latter flask should be used, however, for oxidising organic matter when present. E. G.

Detection of Free Carbon Dioxide (in Water). L. W. Winkler (*Zeitsch. angew. Chem.*, 1915, **28**, 376).—In moderately hard waters the presence of free carbon dioxide may be detected by the addition of two drops of 10% copper sulphate solution to 100 c.c. of the water; if the latter does not contain free carbon dioxide the mixture becomes turbid, but if the gas is present in solution the mixture remains clear. If the clear mixture is shaken with air, the carbon dioxide is expelled, and a turbidity develops; should a turbidity not form under these conditions, the water contains a non-volatile acid (humic acid) or a large quantity of organic matter. The copper sulphate test fails, however, in the case of soft waters. Free carbon dioxide in this kind of water may be detected by mixing ten drops of a 1% alizarin solution (in alcohol) with 100 c.c. of the water. A bluish-red coloration indicates the absence of free carbon dioxide; copper-red, a small quantity; reddish-yellow, a moderate quantity; yellow, a large quantity. W. P. S.

Estimation of Carbon Dioxide in Ordinary Natural Waters. Alfredo Cavazzi (*Ann. Chim. applicata*, 1915, **4**, 81—91).—The total carbon dioxide in waters is estimated by heating the water with dilute sulphuric acid, absorbing the liberated carbon dioxide in an ammoniacal solution of calcium chloride, and determining the amount of calcium carbonate thus formed by dissolution in excess of standard acid solution and titration with sodium hydroxide solution in presence of methyl-orange. The special apparatus employed and the details of the procedure followed are fully described.

The combined carbon dioxide is estimated as follows: Two litres of the water are shaken with 1 gram of finely powdered hydrated calcium sulphate or selenite and 0·1—0·2 gram of sodium chloride until the calcium sulphate is dissolved, the magnesium hydrogen carbonate being converted into calcium carbonate; the sodium chloride renders more stable any magnesium chloride present. The liquid is then evaporated to dryness in a porcelain dish of about 0·5 litre capacity, first over a naked flame and finally on a water-bath. The calcium carbonate is then dissolved in 50 c.c. of standard, approximately $N/2$-hydrochloric acid, and the solution filtered to separate the undissolved gypsum, dish and filter being washed with cold water and the liquid titrated with sodium hydroxide in presence of methyl-orange. The only objection to this method is that, during the evaporation, the calcium carbonate may be slightly attacked by any small amount of dissolved silica present in the water.

The free and semi-combined carbon dioxide may be estimated indirectly by difference or directly by heating the water (2 litres) with a few pieces of pumice and 1·5 grams of finely powdered hydrated calcium sulphate in the apparatus used for estimating the total carbon dioxide. The carbon dioxide liberated is collected, as before, in ammoniacal calcium chloride solution, and the calcium carbonate formed determined by titration.

The results obtained by the above method with water from the new aqueduct at Bologna are: total carbon dioxide, 0·1700; combined, 0·0835; and free and semi-combined, 0·0872 gram per litre.

T. H. P.

Rapid Method for the Detection of Poisonous Minerals in Water. E. Fleury (*J. Pharm. Chim.*, 1915, [vii], **12**, 215—220).—The following tests may be employed for the detection of injurious metals, etc., in clear, filtered water; any water which, after filtration, exhibits a distinct colour should be rejected as unfit for drinking. A test-tube is filled with the water, and two drops of 10% sodium sulphide solution are added; if the mixture remains clear, two drops of hydrochloric acid are added, when the formation of a yellow precipitate indicates the presence of arsenic. A fresh quantity of the water is then tested with saturated strontium sulphate solution for the detection of barium salts. If sodium sulphide produces a coloration or precipitate, the addition of hydrochloric acid will discharge the colour or dissolve the precipitate if due to the presence of iron or zinc, the former giving a black precipitate and the latter a white precipitate. Should the colour or precipitate not disappear on the addition of hydrochloric acid, the colour will indicate to some extent the metal present; it will be yellow with cadmium, orange with antimony, and black with mercury, copper, lead, silver, bismuth, or tin. The presence of cyanides is detected by heating the water with a few drops of hydrochloric acid in a test-tube, a strip of sodium picrate paper being suspended in the upper part of the tube; the paper is coloured reddish-brown if hydrocyanic acid (cyanide) is present. Nitro-

prussides are detected by adding a drop of sodium sulphide solution to the water. W. P. S.

Arsenious Oxide as an Alkalimetric Standard. Alan W. C. Menzies and F. N. McCarthy (*J. Amer. Chem. Soc.*, 1915, **37**, 2021—2024).—Menzies and Potter (A., 1912, ii, 1166) have described a method for the accurate estimation of arsenic acid. Arsenious oxide can be readily obtained in a pure condition, and is therefore serviceable as a standard in volumetric analysis. Moreover, it can easily be converted quantitatively into arsenic acid by the action of nitric acid, and a standard solution of arsenic acid can therefore be prepared without difficulty. It is shown that such a solution can be used for the estimation of alkali in presence of phenolphthalein. E. G.

Potassium Hydrogen and Sodium Hydrogen Phthalates as Standards in Acidimetry and Alkalimetry. W. S. Hendrixson (*J. Amer. Chem. Soc.*, 1915, **37**, 2352—2359).—Dodge (this vol., ii, 102) has recommended potassium hydrogen phthalate for standardising alkali solutions, and has suggested that sodium hydrogen phthalate might also be of service for the same purpose.

A standard solution of hydrochloric acid was prepared by diluting the acid of constant b. p. in accordance with Hulett and Bonner's method (A., 1909, ii, 342), and was used for the standardisation of a solution of sodium hydroxide. By means of the latter solution, the hydrochloric acid was standardised against benzoic acid, potassium hydrogen phthalate, and sodium hydrogen phthalate. The concentration of the hydrochloric acid was also estimated by the silver chloride method. The results agree very closely, but a slightly lower value was obtained by Hulett and Bonner's standard than by any of the other methods (compare Morey, A., 1912, ii, 986).

The alkali hydrogen phthalates are very suitable as standards, and are preferable to benzoic acid on account of their high molecular weight, their greater solubility, and the fact that they can be easily and rapidly prepared in a pure state. E. G.

Estimation of Small Quantities of Silver by Cyanimetry. G. Rebière (*Bull. Soc. chim.*, 1915, [iv], **17**, 306—309).—The author finds that, by working in the dark and illuminating the titration bottle, thereby rendering the opalescent colloidal precipitate of silver iodide readily visible, it is possible to apply Denigès' cyanimetric method to the estimation of small amounts of silver, using $N/100$ solutions, the error being reduced to about 0·05 mg. W. G.

Two Methods of Separation of the Metals of the Alkaline Earth Group. Alice G. Paterson (*J. Amer. Chem. Soc.*, 1915, **37**, 2346—2352).—If a solution of salts of the alkaline-earth metals is treated with excess of solutions of ammonium carbonate and sulphate, barium is precipitated as sulphate and calcium and

strontium as carbonates. The mixture is heated until it boils, and left for twenty to thirty minutes, and occasionally stirred. The precipitate is collected, washed, and boiled with 1% acetic acid. After removing the barium sulphate by filtration, the filtrate is rendered slightly alkaline with ammonia, treated with a mixture of ammonium carbonate and oxalate, heated until it boils, and left for twenty to thirty minutes, with occasional stirring. The precipitate of calcium oxalate and strontium carbonate is treated with 1·5% acetic acid and filtered. The residue consists of calcium oxalate. The filtrate is made alkaline with ammonia, and the strontium precipitated with ammonium sulphate or carbonate.

Another method of separation is described in which the solution is heated with ammonium chloride and sulphate. Barium and strontium, and perhaps a little calcium, are precipitated as sulphates, but most of the calcium remains in solution. The precipitate is collected, warmed with lead acetate solution, and the mixture is filtered. The residue consists of lead and barium sulphates, and the filtrate contains strontium acetate, the excess of lead acetate, and perhaps a little calcium acetate. The filtrate is freed from lead by means of hydrogen sulphide, and tested for strontium. E. G.

Composition and Analysis of Lime-Sulphur Liquors. J. Bodnár (*Chem. Zeit.*, 1915, **39**, 715—716).—The lime-sulphur solutions used as insecticides in agriculture contain chiefly calcium polysulphides and calcium thiosulphate, together with a very small quantity of calcium sulphate (compare A., 1908, ii, 380); the presence of calcium sulphite in the solution is improbable, since sulphites react with sulphides, with the formation of thiosulphate. The solutions contain per 100 c.c.: sulphur as thiosulphate, 2·84 to 3·50 grams; as polysulphides, 10·20 to 16·29 grams; as sulphide, 2·84 to 3·61 grams; as sulphate, 0·1 gram. Concentrated solutions are also sold; these contain sulphur as polysulphide, 31·26 to 33·80 grams, and as thiosulphate, 1·85 to 1·92 grams. A method for the estimation of the polysulphide and thiosulphate sulphur in these solutions depends on the reactions shown in the following equations: (1) $CaS_4 + 2AgNO_3 = Ag_2S + 3S + Ca(NO_3)_2$ and $CaS_5 + 2AgNO_3 = Ag_2S + 4S + Ca(NO_3)_2$; (2) $CaS_2O_3 + 2AgNO_3 = Ca(NO_3)_2 + Ag_2S_2O_3$ and $Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4$. Ten c.c. of the sample are diluted to 100 c.c., and 10 c.c. of this solution are added to a mixture of 50 c.c. of $N/10$ silver nitrate solution and 20 c.c. of water; the mixture is shaken, diluted to 100 c.c., and filtered, the filtrate being collected in a dry flask. The latter is then removed, the precipitate is washed with warm water, dried at 100° and weighed. Fifty c.c. of the filtrate are treated with 30 c.c. of $N/10$ sodium chloride solution and 15 c.c. of $N/10$ sodium hydroxide solution, phenolphthalein is added, and the mixture titrated with $N/10$ sulphuric acid; potassium chromate solution is then added, and the mixture titrated with $N/10$ silver nitrate solution. The amounts of sulphur present as thiosulphate and sulphide, in grams per 100 c.c. of the solution, are found from

the formulæ: thiosulphate sulphur, $t = 100 \times 4(a-b) \times 0{\cdot}0016035$; sulphide sulphur, $s = 100 \times 2(25 + c - d) \times 0{\cdot}0016035$, where a = c.c. of $N/10$ sodium hydroxide solution, b = c.c. of $N/10$ sulphuric acid, c = c.c. of $N/10$ silver nitrate solution, d = c.c. of $N/10$ sodium chloride solution. The sulphur present as polysulphide is found from the equation: polysulphide sulphur, $p = 100e - 7{\cdot}727(s + t/2)$, where e = weight of the precipitate. In some cases, sodium chloride is used in the preparation of the solution, and its quantity must be estimated and the corresponding quantity of silver chloride subtracted from p. The sodium chloride is estimated by rendering 20 c.c. of the diluted (10%) sample ammoniacal, adding hydrogen peroxide, boiling the mixture until the excess of hydrogen peroxide has been decomposed and all ammonia expelled, and titrating the solution with $N/10$ silver nitrate solution. W. P. S.

Blacher's Method for Estimating Hardness in Water. P. A. Meerburg (*Chem. Weekblad.*, 1915, **12**, 920—924).—Blacher's method for estimating the hardness of water yields satisfactory results, but for hardness exceeding 20° the sample should be diluted. A. J. W.

The Iodide Method Applied to the Estimation of Copper in the Presence of Tin. Robert W. Coltman (*J. Ind. Eng. Chem.*, 1915, **7**, 764—766).—A quantity of the copper–tin alloy, containing not more than 0·25 gram of copper, is heated in a flask with 15 c.c. of nitric acid (2:1) until decomposition is complete; 3 c.c. of concentrated sulphuric acid diluted with water are then added, and the mixture evaporated. When all nitric acid has been expelled and sulphuric acid fumes appear, stannic and cupric sulphates separate suddenly as a crystalline mass. The flask is then removed immediately from the flame, its contents cooled, treated with 25 c.c. of water, and again evaporated until fumes appear. The residue is dissolved in 50 c.c. of cold water, a further 25 c.c. of water and 10 c.c. of 40% potassium iodide solution are added, and the solution is titrated with $N/10$ thiosulphate solution. The presence of small quantities of lead (that is, up to 8%) in the alloy does not interfere with the estimation, but antimonic and ferric salts should not be present in the solution. W. P. S.

Analysis of Turbadium Bronze. Howell Williams (*Chem News*, 1915, **112**, 175—176).—Turbadium bronze, which is used for solid propeller castings, has the following approximate composition: Cu, 48; Zn, 46·45; Sn, 0·50; Pb, 0·10; Fe, 1·0; Al, 0·20; Mn, 1·75; Ni, 2·00. These metals are conveniently estimated in the following order: Tin, as dioxide, by dissolving the drillings in nitric acid (D 1·2), concentrating to 10 c.c., and diluting with water. Copper electrolytically in the filtrate from the tin precipitate, using platinum gauze electrodes with a rotating anode. Lead is dissolved off the anode with nitric acid, and weighed as lead sulphate. Iron, aluminium, and manganese are precipitated from

the mother liquor from the electrolytic separation by bromine water and ammonia in presence of ammonium chloride. The precipitates are dissolved in hot dilute hydrochloric and sulphurous acids, the iron re-oxidised with nitric acid, and separated with the aluminium from the manganese by the ammonium acetate process. The iron in the precipitate is estimated by titration with dichromate after reduction with stannous chloride, and the aluminium is obtained by difference. Manganese is precipitated from the filtrates from the lead sulphate and the ammonium acetate separation with ammonium hypobromite. Zinc is precipitated with ammonium phosphate in acetic acid solution, and nickel from the filtrate with dimethylglyoxime. The totals of 127 analyses have only varied between 99·84 and 99·92%. If more than 1·5% of nickel is present, the zinc must be precipitated twice, as nickel may be carried down in the first precipitates of zinc phosphate.

G. F. M.

Estimation of Aluminium Oxide and Total Aluminium in Steel. F. O. Kichline (*J. Ind. Eng. Chem.*, 1915, **7**, 806—807).—The method depends on the fact that, when it has been heated at the temperature of molten steel, aluminium oxide is practically insoluble in dilute hydrochloric acid. Fifty grams of the drillings are warmed with a mixture of 200 c.c. of hydrochloric acid and 300 c.c. of water; the insoluble portion is collected on a filter, washed, and ignited in a platinum crucible. The ignited residue is fused with 0·5 gram of anhydrous borax, 5 grams of sodium carbonate are then added, the heating is continued for a few minutes, the mass next dissolved in water, and the aluminium oxide estimated in the usual way. The aluminium in the hydrochloric acid filtrate is precipitated as phosphate, the precipitate is dissolved in nitric acid, the solution boiled with permanganate to oxidise chromium, and the aluminium precipitated by the addition of ammonia; this precipitate is dissolved in hydrochloric acid, the solution evaporated to dryness to separate silica, and the aluminium precipitated finally as phosphate.

W. P. S.

Ignition of Ferric Oxide in Gravimetric Estimation of Iron. Emmerich Selch (*Zeitsch. anal. Chem.*, 1915, **54**, 457—463).—Alumina before being weighed must be subjected to an intense heat over the blowpipe. If, now, also ferric iron is present, there is a supposed danger of a slight reduction of the same.

The author, however, has found that if care is taken not to allow the flame to play over the top of the crucible, thus preventing the action of reducing gases, the blowpipe may be safely used without any fear of iron oxide being reduced.

L. de K.

Reduction of Ferric Iron Solutions Prior to Titrating with Permanganate. Alfred Hoenig (*Zeitsch. anal. Chem.*, 1915, **54**, 441—457).—A criticism of the methods usually employed (use of zinc, aluminium, magnesium, silver, stannous chloride, etc.). The following modification of the stannous chloride method is recommended.

About 0·11 gram of hæmatite, 0·25 gram of other iron ore, 0·5 gram of bauxite, or 5 grams of limestone are operated on. The final filtrate should occupy about 50 c.c., and contain about 10 c.c. of free hydrochloric acid. After heating the solution in a measuring flask, stannous chloride solution is slowly added until the liquid is quite decolorised; a large excess of the reagent should be avoided. Two grams of flowers of sulphur are now introduced, and the whole is boiled for one to two hours in a current of carbon dioxide; the water evaporating should be frequently replenished. When cold, the whole is made up to the mark, and an aliquot part of the clear liquid is transferred to a flask already containing 100 c.c. of water and 25 c.c. of manganese solution, and slightly tinged with permanganate, and the whole is now titrated with standardised permanganate (1 c.c. = 0·0027843 gram of ferric oxide).

The manganese solution is prepared by dissolving 170 grams of crystallised manganese sulphate in water, adding 400 c.c. of phosphoric acid (D 1·7) and 340 c.c. of sulphuric acid (D 1·8). The whole is then diluted with water to 2·5 litres. L. DE K.

Qualitative Detection and Separation of Platinum, Arsenic, Gold, Selenium, Tellurium, and Molybdenum. PHILIP E. BROWNING (*Amer. J. Sci.*, 1915, [iv], **40**, 349—350).—Whilst making experiments on the detection and separation of the elements mentioned above by the method due to Noyes and Bray (A., 1907, ii, 391) it was found that the reactions for gold and arsenic were unsatisfactory, and in some cases those for selenium and tellurium were doubtful. The reasons for the difficulties are explained in the paper, and it is shown that if the separation of the arsenic as double arsenate is left until after the removal of gold, tellurium, and selenium, the difficulties will not occur. The filtrate from the tellurium when evaporated with nitric acid or bromine contains the arsenic and molybdenum in a suitable state of oxidation, and the arsenic can then be precipitated with "magnesia mixture." The filtrate from the magnesium ammonium arsenate is then treated with zinc, and a soluble thiocyanate, when red molybdenum thiocyanate is precipitated. The use of oxalic acid in the precipitation of gold may also be substituted by that of hydrogen peroxide. J. F. S.

The Detection of Benzene in Organs and its Distribution in the Organism. GEORG JOACHIMOGLU (*Biochem. Zeitsch.*, 1915, **70**, 93—104).—The benzene is distilled off from a mixture of the organs with dilute sulphuric acid into carbon tetrachloride. This solvent is then separated from the water which distils over, and the solution of the benzene in carbon tetrachloride is nitrated. The dinitrobenzene formed can be directly weighed for a quantitative estimation; for a qualitative test the dinitrobenzene can be detected by means of Chavassieu and Morel's lævulose reaction (A., 1907, ii, 135). It was found that in animals poisoned by benzene, the brain and spinal cord contained relatively more of this substance than the other organs. S. B. S.

The Detection of Small Amounts of Glycerols and of Alcohols and Acids belonging to the Carbohydrate Group. JOHN A. MANDEL and CARL NEUBERG (*Biochem. Zeitsch.*, 1915, **71**, 214—218).—Glycerol is readily oxidised to glycerose by warming with *N*-sodium hypochlorite solution (prepared by Raschig's method); the sugar can then be detected by the orcinol reaction. The following alcohols give the same colour tests after similar treatment: erythritol, adonitol, *l*-arabitol, *d*-mannitol, *d*-sorbitol, dulcitol; also salts of the following acids: *d*-gluconic acid, *d*-mannonic acid (lactone), *d*-galactonic acid; also the following hexoses: dextrose, *d*-mannose, and *d*-galactose, and *d*-glucosamine hydrochloride. S. B. S.

A Colorimetric Method for the Estimation of Phenols and Phenol Derivatives in Urine. OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1915, **22**, 305—308).—Uric acid and traces of any protein are first precipitated with acid silver lactate and colloidal iron. The free phenols in the filtrate are estimated colorimetrically with a phosphomolybdic–phosphotungstic acid reagent and sodium carbonate, and the total phenols after boiling with hydrochloric acid. The standard phenol solution is standardised by iodometric titration. W. D. H.

The Estimation separately of Phenol and *p*-Cresol in Urine. M. SIEGFRIED and R. ZIMMERMANN (*Biochem. Zeitsch.*, 1915, **70**, 124—129).—The authors describe certain modifications in the details of their method (A., 1911, ii, 72 and 941), and now give the method in its final form. S. B. S.

A Qualitative (Reduction) Test for Sugar in Normal Human Urine. OTTO FOLIN (*J. Biol. Chem.*, 1915, **22**, 327—329).—Normal urine is sugar-free so far as the usual tests go, but traces are nevertheless present. In the test proposed a very sensitive alkaline copper solution is used; another consideration is the fact that in presence of copper, alkaline picrate solutions are not reduced by sugar; thus creatinine can be removed by picric acid before the sugar test is applied. The copper solution contains crystallised copper sulphate and glycerol, and is mixed immediately before use with a solution of anhydrous potassium carbonate. On boiling this with creatinine-free urine, positive results were obtained in one hundred cases with normal people (students). W. D. H.

Estimation of Sugar by Reduction of Copper Solutions RAYM. VAN MELCKEBEKE (*Chem. Weekblad*, 1915, **12**, 823—826).—The author finds that in the estimation of sugars more accurate results are obtained by estimating the reduced copper gravimetrically than those given by the volumetric method. A. J. W.

Disturbing Factor in Barfoed's Test. WILLIAM H. WELKER (*J. Amer. Chem. Soc.*, 1915, **37**, 2227—2230).—In an earlier paper (A., 1909, ii, 524) it was stated that small quantities of sodium

chloride interfere with Barfoed's test, a greenish-white precipitate being produced, instead of the red cuprous oxide. Experiments have now been made to determine the concentration of sodium chloride which would interfere with the test in dextrose solutions of various concentrations, and the results are tabulated. If Barfoed's reagent is treated with solution of sodium chloride at the ordinary temperature, a precipitate is produced if the concentration of the salt is 0·32%, but not if the concentration is as low as 0·16%. The presence of dextrose at the ordinary temperature causes the production of opalescent, colloidal solutions. The greenish-white precipitate formed on heating such solutions contains copper, sodium, chlorine, and the acetic acid radicle; its percentage composition has not been determined. E. G.

A Criticism of the Bang and Lewis-Benedict Methods for the Estimation of Blood-sugar with Suggestions for the Modification of the Latter Method. R. G. PEARCE (*J. Biol. Chem.*, 1915, **22**, 525—533).—Bang's method was found unsatisfactory in many particulars, and modifications are suggested to improve it. The Lewis-Benedict method was found to be excellent; to avoid boiling and consequent loss, heating under pressure in the autoclave is recommended. W. D. H.

Estimation of Raffinose by Enzymotic Hydrolysis. C. S. HUDSON and T. S. HARDING (*J. Amer. Chem. Soc.*, 1915, **37**, 2193—2198).—It has been shown by Hudson (A., 1914, i, 1147) that from top-fermentation yeast an extract can be prepared containing invertase, but no melibiase, and from bottom yeast an extract containing both enzymes. The former extract hydrolyses raffinose with production of melibiose and lævulose, whilst the latter extract converts it into galactose, dextrose, and lævulose. A method based on these facts has been devised for estimating raffinose.

For the analysis of a mixture of raffinose and sucrose the solution is first treated with top-yeast solution, and left until the rotation becomes constant. At this stage all the sucrose has been inverted, and all the raffinose hydrolysed to melibiose and lævulose. Bottom-yeast extract is now added to the solution, the rotation is determined immediately afterwards, and the solution is then left at the ordinary temperature and the rotation measured from day to day. A change of rotation in the lævo-direction indicates the hydrolysis of melibiose. In a 20 cm. tube a solution containing 1 gram of melibiose per 100 c.c. will change its rotation during hydrolysis to the extent of 4·18° Ventzke, whence each degree indicates 0·239 gram of melibiose per 100 c.c., corresponding with 0·352 gram of anhydrous raffinose. The percentage of raffinose may thus be estimated.

The method has been applied to the estimation of raffinose in admixture with sucrose, sucrose and dextrose, lævulose, invert-sugar, lactose, maltose, cellose, and trehalose, and in all cases satisfactory results were obtained. E. G.

The Colour Reactions of Trioses and Methylglyoxal. CARL NEUBERG (*Biochem. Zeitsch.*, 1915, **71**, 150—157).—Glyceraldehyde and dihydroxyacetone can be distinguished from one another in that only the latter yields a positive phloroglucinol reaction. Both give a positive orcinol reaction. Glyceraldehyde can be distinguished from the pentoses and glycuronic acid in that it does not give the phloroglucinol reaction. Dihydroxyacetone, but not glyceraldehyde, gives the resorcinol reaction. Methylglyoxal behaves in quite a different manner. It yields neither the orcinol nor phloroglucinol reactions, and its reaction with resorcinol is not typical; on the other hand, it gives with sodium nitroprusside and alkali or organic bases (secondary amines) a bright red colour, which is changed to a violet colour by acetic acid. This reaction is quite different from that given by glyceraldehyde and dihydroxyacetone. S. B. S.

The Estimation of Lactic Acid in the Presence of Pyruvic Acid. LUDWIG CZAPSKI (*Biochem. Zeitsch.*, 1915, **71**, 167—168).—In the method given by Embden and Oppenheimer (A., 1913, i, 1275) sodium hydrogen sulphite is added to the aqueous solution of the acids, and the mixture is then extracted with ether. It is now shown that the amount of the hydrogen sulphite employed by Embden and Oppenheimer is insufficient to prevent extraction by the ether of pyruvic acid; this amount should be doubled. Attention is called to the similarity of the zinc salts of pyruvic and racemic acids, which are liable to be mistaken for one another. S. B. S.

The Estimation of Lactic Acid in Urine. J. SCHNEYER (*Biochem. Zeitsch.*, 1915, **70**, 294—298).—Meissner's method (this vol., ii, 187) of treating the lactic acid with sulphuric acid and measuring the carbon monoxide evolved was applied to the estimation of this acid in urine. Oxalic acid must be first separated by calcium chloride; the urine is then concentrated to a syrup, acidified with phosphoric acid, and then mixed with plaster of Paris. From the powder thus obtained the lactic acid is extracted by ether. S. B. S.

Titration of Tartaric Acid with Permanganate. REGINALD S. DEAN (*Chem. News*, 1915, **112**, 154—155).—Tartaric acid may be titrated with permanganate by the following method: The solution of tartrates is acidified with 3 c.c. of nitric acid, and titrated to a permanent pink. The solution is then neutralised, zinc nitrate is added, and the whole is titrated, boiling, with permanganate, as in the Volhardt method. Under these conditions the tartaric acid is oxidised completely to carbon dioxide and water, and fairly accurate results may be obtained. The oxidation in acid solution only required about two-thirds of the permanganate which would be necessary for the complete oxidation, and some tests indicated that the intermediate compound was formic acid, which was further oxidised during the second part of the titration in neutral solution. G. F. M.

Characteristic Reaction of Picric Acid. G. RODILLON (*J. Pharm. Chim.*, 1915, [vii], **12**, 177—179).—A small quantity of the solution to be tested for picric acid is mixed with one-fourth its volume of hydrochloric acid, and a few fragments of zinc are added; after a short time the solution is decanted into a test-tube, mixed with ten drops of hydrogen peroxide, and ammonia is poured on to the surface of the mixture. A coloured zone appears at the junction of the two liquids if picric acid was present in the original solution; the upper part of this zone has a bluish-violet coloration, and the lower a reddish-violet. The bluish-violet colour is characteristic of picric acid. In testing urine, beer, etc., for picric acid, the liquid should be acidified with hydrochloric acid, extracted with ether, the ethereal extract evaporated, and the residue thus obtained used for the test. W. P. S.

Detection of Picric Acid in Urine. P. GRÉLOT (*J. Pharm. Chim.*, 1915, [vii], **12**, 209—215).—One hundred c.c. of the urine are treated with 10 c.c. of normal lead acetate solution, the mixture is filtered, excess of lead is removed as sulphate from the filtrate, and the solution then extracted with ether; the ethereal solution dyes wool yellow or orange, according to the proportion of picramic acid present. The residue obtained on evaporating the ethereal solution is boiled for a few minutes with the addition of 33% sulphuric acid to oxidise the picramic acid, the mixture then neutralised, and the usual tests for picric acid are applied. Alternatively, the residue from the ethereal solution may be dissolved in 3 c.c. of hydrochloric acid, and the solution heated gently after the addition of a small piece of tin; a colourless solution is obtained, which develops a blue coloration when diluted with twenty times its volume of water. The appearance of the blue colour may be hastened by the addition of a drop of ferric chloride solution. If the reduced solution is extracted with ether, the ethereal solution exhibits a blue coloration after exposure to air. In most cases the urine may be acidified with hydrochloric acid, extracted with ether, and the ethereal solution tested with a thread of wool, but it must be noted that biliary pigments also colour the wool yellow; this colour is removed by washing with soap and water, whilst the yellow-orange colour of wool dyed with picric and picramic acids is permanent. W. P. S.

Estimation of Lecithin in Small Amounts of Blood. W. R. BLOOR (*J. Biol. Chem.*, 1915, **22**, 133—144).—The method which is described with full details consists in the extraction of the phosphatides from blood or serum with warm alcohol–ether, and the estimation of their amount by precipitation of the phosphoric acid after ashing as the silver salt, or the silver ammonium salt. The phosphate is precipitated by silver nitrate in faintly alkaline solution in the presence of ammonium salts, and the amount of the precipitation measured by the nephelometer. The method has an accuracy of about 2%. W. D. H.

Estimation of Volatile Esters in Citrus Oils and Extracts. ALAN R. ALBRIGHT and CHARLES O. YOUNG (*J. Amer. Chem. Soc.*, 1915, **37**, 2382—2387).—The following method has been devised for the estimation of esters in citrus oils. A sample of about 100 c.c. is taken, and the terpenes are removed by distillation under 2—5 mm. pressure. The residual oil is distilled in a current of steam, the aldehydes in the distillate are converted into their semicarbazones, and the esters are then estimated by hydrolysis with potassium hydroxide in presence of the semicarbazones. In the examination of extracts, the readily volatile matter is removed by distillation and treated in the same way as the product obtained by distillation in steam in the case of the oils. E. G.

Estimation of Thiophen in Benzene. V. PAOLINI and B. SILBERMANN (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 206—210).—Dimroth (A., 1902, i, 656) found that the mercury-halogen residue, ·HgX, of aromatic mercury compounds is readily replaceable by a halogen atom. In accord with this observation, when the tetramercuri-compound obtained by the action of saturated mercuric acetate solution on thiophen (compare Paolini, A., 1907, i, 788) is converted by means of sodium chloride into the corresponding mercurichloride, and the latter compound shaken with a solution of iodine in potassium iodide, the changes occurring are expressed by the scheme $R\cdot Hg\cdot OAc \longrightarrow R\cdot HgCl \longrightarrow RI + HgClI$. The resultant product is not, however, pure tetraiodothiophen, but consists of a mixture of the latter with di-iodothiophen. The conclusion is drawn that the action of saturated mercuric acetate solution on thiophen yields a mixture of thiophen di- and tetramercuriacetates in proportions varying with the temperature, concentrations, etc. The conditions have been established for the preparation of the pure tetramercuriacetate.

Tetra-iodothiophen, C_4I_4S, forms an odourless, tasteless, pale yellow, crystalline powder, m. p. 198°, and has the normal molecular weight in boiling carbon tetrachloride.

The following method for the estimation of thiophen in benzene gives good results. A little more than the calculated quantity of mercuric oxide is dissolved in glacial acetic acid, and the liquid cooled, mercuric acetate being deposited. The benzene to be tested is then added, and the mixture heated on a boiling water-bath for about fifteen minutes. The precipitate formed, consisting solely of thiophen tetramercuriacetate, is separated from the cold liquid, washed several times with ether, dried at 100° and weighed. T. H. P.

Formaldehyde Micro-titration and its Applications in Physiology. A. CLEMENTI (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 51—55).—See this vol., i, 1025.

The Behaviour of 2 : 5-Diketopiperazines in Formalin Titrations. P. GLAGOLEV (*Biochem. Zeitsch.*, 1915, **70**, 119—123).—The diketopiperazines do not react to Sörensen's formalin titra-

tion. The following substances were investigated: glycine anhydride, lactimide, tyrosine anhydride, and glycyl-leucine anhydride. S. B. S.

The Diazo-reactions of Histidine and Tyrosine. GINSABURO TOTANI (*Biochem. J.*, 1915, **9**, 385—392).—Both substances give similarly coloured diazo-compounds; when reduced by zinc dust, that of tyrosine gives a rose-red, that of histidine a golden-yellow coloration; the latter reaction is specific for this amino-acid among protein products, and is most characteristic in solutions stronger than 1 in 20,000, but is recognisable down to 1 in 100,000. The tyrosine reaction is not specific, but the original diazo-reaction is confined to tyrosine and histidine. The delicacy is 1 : 10,000, and the test is superior to Millon's, especially in the presence of chlorides. The red coloration given by tyrosine and other amino-acids in the secondary reaction is destroyed by oxidation, resulting in nearly colourless solutions. The yellow due to histidine is a little weakened. Using a small amount of diazobenzenesulphonic acid sufficient only to couple with the histidine, or applying oxidation by hydrogen peroxide in conjunction with the reduction, the presence of histidine in proteins can be easily detected by the colour of the secondary diazo-reaction. W. D. H.

New Colour Reaction for Papaverine. L. E. WARREN (*J. Amer. Chem. Soc.*, 1915, **37**, 2402—2406).—If papaverine ferricyanide is treated with Marquis' reagent, a blue coloration is produced, which changes to violet, green, and finally to brownish-yellow. The same effect is obtained if Marquis' reagent is added to a mixture of papaverine and potassium ferricyanide. Many other oxidising agents can be used instead of potassium ferricyanide, but the shades of colour produced vary to some extent with the reagent. The test is best carried out by mixing the alkaloid with a small quantity of an oxidising agent, such as cerium oxide, phosphomolybdic acid, or potassium permanganate, and a few drops of sulphuric acid containing a little formaldehyde, and stirring the mixture.

The test was applied to thirty-nine alkaloids, and only one, a sanguinaria alkaloid, gave a coloration resembling that furnished by papaverine. If, however, selenious acid is used as the oxidising agent, the sanguinaria alkaloid yields an intense, purplish-violet coloration instead of the blue given by papaverine. E. G.

Gravimetric Assay of Tanning Materials. A. GAWALOWSKI (*Zeitsch. anal. Chem.*, 1915, **54**, 403—405).—Fifty grams of oak bark are digested for one day in a corked flask with 250 c.c. of alcohol-ether mixture (1 : 2). Ten c.c. are evaporated at 40° in a porcelain dish, the residue is taken up with 50 c.c. of water, and in 25 c.c. of the filtrate (1 gram) the tannins are precipitated with solution of copper acetate. The precipitate is collected on a weighed filter, washed, dried in the water-oven, and weighed. As the amount of copper contained therein is very variable for various

tannins, and not even constant for the same material, the tannins cannot be obtained by calculation, but the content in metallic copper must be determined by incineration in oxygen and subsequent heating in hydrogen. The difference equals tannins. In accurate analyses, an allowance should be made for hydrogen displaced by copper.

In the case of other materials, 15 grams are treated with 150 c.c. of the alcohol-ether mixture. When assaying "extracts," 10 grams are shaken with 200 c.c. of the solvent, and the analysis is carried out as stated above. L. DE K.

Method of Estimating Proteolytic Enzymes. BICE NEPPI (*Boll. Chim. Farm.*, 1915, **54**, 289—297).—In view of the insufficient and inaccurate methods given in the Italian and other pharmacopœias for the estimation of the activities of preparations of pepsin and pancreatin, the author suggests the use of the following methods.

For pepsin, a modification of Fuld and Levison's method (A., 1908, ii, 76) is recommended, the solutions required being $N/300$-hydrochloric acid, 30% sodium chloride solution, and a solution containing 1 gram of edestin in 1000 c.c. of $N/300$-hydrochloric acid. Into each of a series of test-tubes, not more than 1 cm. in width, are introduced 2 c.c. of the edestin solution, 0·9, 0·8, . . . 0 c.c. of $N/300$-hydrochloric acid, and 0·1, 0·2, . . . 1·0 c.c. of the pepsin solution. The tubes are kept at 22—23° for thirty minutes, and to each is then added about 1 c.c. of the sodium chloride solution. The first tube of the series, in which no turbidity appears, corresponds with complete digestion of the edestin. If this occurs with 0·5 c.c. of a 0·1% solution of pepsin, 0·0005 gram of the latter is sufficient to digest 2 mg. of edestin, and the activity of the pepsin will be $2/0·0005 = 4000$ units. The hydrochloric acid and the pepsin solution should be added to the tubes in the same order.

In the case of pancreatin, a modified form of Gross's method (A., 1908, i, 234) is employed. One gram of pure casein is dissolved in the hot in 1 litre of 0·1% sodium carbonate solution, and 10 c.c. of chloroform subsequently added. Increasing quantities of the enzyme solution are then added to a series of tubes, each containing 10 c.c. of the casein solution, the volumes equalised by addition of water, and the tubes kept at 40° for fifteen minutes. To each tube is then added 1 c.c. of a solution of 5 c.c. of acetic acid in 50 c.c. of water and 45 c.c. of 95% alcohol. If 0·4 c.c. of a 0·1% pancreatin solution is just able to digest 10 c.c. of the casein solution, the activity of the pancreatin is expressed as $10/0·0004 = 25{,}000$ units, 1 gram of the pancreatin being capable of digesting 25 grams of casein. T. H. P.

General and Physical Chemistry.

Theory of Solutions. The Influence of Change of Volume on Specific Refraction in Mixtures of Liquids. JOHN HOLMES (T., 1915, **107**, 1471—1477. Compare T., 1913, **103**, 2165).—Further evidence is advanced in support of the view that deviations from additive relations in the refractive indices of binary liquid mixtures follow closely the corresponding changes in volume. For mixtures of methyl alcohol and water and of *n*-propyl alcohol and water, the ratio of the percentage change in volume to the difference between the observed and calculated refractive indices is very nearly constant, varying only from 290 to 300. The data for mixtures of ethyl iodide and ethyl acetate, benzene and acetic acid, carbon disulphide and acetone, also show that the above ratio is fairly constant, the mean value being 140. These three pairs of liquids exhibit expansion on mixing, whereas contraction takes place in the two alcohol water mixtures.

By application of the method described in previous papers, it is shown that the changes in volume and refractive index give values for the relative complexities of the several liquids which are identical with those recorded previously. H. M. D.

Refractive and Dispersive Power of Silicon in Organic Silicon Compounds. ARTUR BYGDÉN (*Zeitsch. physikal. Chem.*, 1915, **90**, 243—252).—The refractive indices of a large number of silico-organic derivatives have been determined at temperatures between 15·5° and 25·7°, using a large Pulfrich refractometer. Density determinations have been made for the same substances at 10°, 20°, and 30°. The refractive indices were measured for the wave-lengths of the *C*, *F*, and *G* hydrogen lines and the *D* sodium line. The following silico-hydrocarbons were measured: tetramethylsilicane, trimethylethylsilicane, trimethyl-*n*-propylsilicane, dimethyldiethylsilicane, trimethyl-*n*-butylsilicane, dimethylethyl-*n*-propylsilicane, trimethyl*iso*amylsilicane, dimethylethyl*iso*butylsilicane, tetraethylsilicane, triethyl-*n*-propylsilicane, triethyl-*n*-butylsilicane, triethyl*iso*butylsilicane, triethyl*iso*amylsilicane, hexamethylsilicoethane, *cyclo*pentyldimethylsilicane, phenyltrimethylsilicane, phenyldimethylethylsilicane, benzyltrimethylsilicane, and phenyltriethylsilicane. The value of the atomic refraction of silicon calculated from these compounds varies between 7·03 and 8·04 for the red hydrogen line, the lowest values being obtained from tetramethyl- and tetraethyl-silicane. The following alkyl and aryl silicon chlorides were also measured: trichloroethylsilicane, trichloro-*n*-propylsilicane, trichloro-*n*-butylsilicane, trichlorophenylsilicane, benzyltrichlorosilicane, ethyl-*n*-propyldichlorosilicane, dichloroethyl*iso*butylsilicane, and dichloro*cyclo*pentylsilicane. In the case of these compounds, a much lower atomic refraction was obtained for silicon (5·59—5·99) for the red hydrogen line. A

comparison of the molecular refractions of the silicon compounds with corresponding carbon compounds is made, and it is shown that the replacement of a carbon atom by silicon raises the molecular refraction by about 5 units (5·00—5·30 for the *D* line). The atomic refraction of silicon is also calculated from the results of Martin (T., 1914, **105**, 2836, 2860), and a value obtained which varies between 3·76 and 7·02, the former value being obtained from the compound $Si_2Cl(OEt)_3$ and the latter from Si_3Cl_8. J. F. S.

The Effect of the Electric Field on Spectral Lines. VI. Polarisation and Intensification of a Series. J. STARK (*Ann. Physik.*, 1915, [iv], **48**, 210—235. Compare this vol., ii, 498).—It has been found that the third subordinate series of lithium lines is intensified and polarised when the centres of emission are subjected to the action of a strong electrical field. In the arrangement of apparatus employed in these experiments, the canal rays from an oxygen discharge tube were made to impinge upon an auxiliary electrode covered with lithium chloride. This auxiliary electrode was placed behind the cathode and was connected with the positive pole of the battery, whilst the cathode was connected up with the negative pole. In these circumstances, the canal rays are retarded, whilst the positive lithium ions which are generated between the electrodes of the stationary field are directed towards the cathode.

The fact that the lithium lines of the third subordinate series are intensified so greatly under the influence of an electric field, and that the lines obtained under these conditions are polarised, is considered to show that the electronic vibrations which give rise to this series of lines are parallel to the principal electric axis of the atom.

The new series of helium lines, recently described by Koch (this vol., ii, 713), is supposed to be of the same type as the lithium series which has been examined in detail by the author.

H. M. D.

The Infra-red Emission Spectrum of the Mercury Arc. J. C. MCLENNAN and RAYMOND C. DEARLE (*Phil. Mag.*, 1915, [vi], **30**, 683—695).—The infra-red region of the mercury spectrum has been examined by the use of a Rubens thermopile in combination with a Paschen galvanometer. The results show the existence of thirteen lines between $\lambda=1{\cdot}00\,\mu$ and $\lambda=3{\cdot}02\,\mu$. Considerable differences are found when these are compared with the lines recorded by previous observers.

The lines $\lambda=1{\cdot}038\,\mu$, $\lambda=1{\cdot}270\,\mu$, and $\lambda=3{\cdot}02\,\mu$ exhibit differences of frequency which are identical with the differences characteristic of the triplets in the mercury arc spectrum given by $\nu=2$, $p-m$, d and $\nu=2$, $p-m$, s. The lines $\lambda=1{\cdot}09\,\mu$ and $1{\cdot}367\,\mu$ are possibly the third and second members of a similar triplet with its first member in the neighbourhood of $\lambda=3{\cdot}70\,\mu$. H. M. D.

The Absorption Spectra of Mercury, Cadmium, and Zinc Vapours. J. C. MCLENNAN and EVAN EDWARDS (*Phil. Mag.*, 1915, [vi], **30**, 695—700).—The absorption spectra of the non-luminous

vapours of mercury, cadmium, and zinc show strong symmetrically spaced bands at λ 1849·6, λ 2288, and λ 2139·3, respectively, and narrow, sharply defined bands at λ 2536·72, λ 3260·17, and λ 3075·99, respectively. In addition, the mercury spectrum shows a diffuse, complex band at λ 2338, for which there are no analogues in the cadmium and zinc spectra. The three pairs of corresponding bands are the first members of series represented by $\nu = 1·5$. $S - m$, P, or $\nu = 2$, $p_2 - m$, S. H. M. D.

The Spectra of Ruthenium, Columbium, and Thulium. Emil Paulson (*Physikal. Zeitsch.*, 1915, **16**, 352—354).—To the 548 lines in the spectrum of ruthenium which fall into sixty-five groups of eighteen lines showing constant differences in frequency (compare this vol., ii, 197), the author now adds a further list of ninety-one lines which fall into similar groups. The spectrum of columbium contains thirty-one more or less complete groups of five lines showing wave-number differences equal to 720·25, 1027·02, 355·19, and 303·29, respectively. The thulium spectrum contains seventeen pairs of lines with a constant difference in wave-number equal to 237·00. H. M. D.

The Electron Theory in Organic Chemistry. N. P. McCleland (*Phil. Mag.*, 1915, [vi], **30**, 665—675. Compare this vol., ii, 34).—In a further discussion of the absorption spectra of organic substances on the basis of the atomic model described in the previous paper, it is shown that if a molecule contains two vibration centres, for which the coefficient of mutual induction is small, the absorption bands of the molecule will be the bands of the centres superimposed, with little or no change in position.

It is also shown that the model of the atom is consistent with the stereochemical relations exhibited by ethylene compounds of the type $CR_1R_2{:}CR_3R_4$, and that it may be applied to the structural formula of benzene. H. M. D.

The Optical Rotatory Power of Derivatives of Succinic Acid in Aqueous Solutions of Inorganic Salts. III. George William Clough (T., 1915, **107**, 1509—1519).—In continuation of previous work (T., 1914, **105**, 49; 1915, **107**, 96), the influence of hydrogen chloride, sodium hydroxide, sodium chloride, and barium bromide on the rotatory power of *l*-aspartic acid and of *l*-asparagine in aqueous solution at various temperatures, and for sodium yellow, mercury green, and mercury violet light, has been examined; in the case of *l*-asparagine, the effect of potassium nitrate, iodide, bromide, and chloride, and of ammonium chloride and barium chloride, has also been ascertained. The results are closely analogous in the two cases; thus, hydrogen chloride, sodium chloride, and barium bromide raised the rotation, whilst sodium hydroxide depressed it. Change of temperature affects, in a very similar manner, the rotation of both active compounds in all the solvents employed. The relative effects, on the whole, correspond closely with those observed by Stubbs for malic

acid (T., 1911, **99**, 2265), Patterson and Anderson for ethyl tartrate (T., 1912, **101**, 1833), and the author for tartaric acid (*loc. cit.*). The fact that the changes in the rotatory power of asparagine and aspartic acid are in many respects analogous to those of malic and tartaric acids appears to render a similar explanation necessary in the two cases. The author considers that the influence of inorganic salts on the rotation of aqueous solutions of amino- and hydroxy-derivatives of succinic acid are not due to physical alterations in the molecules of the active compounds, but are to be ascribed to causes of a more chemical character, probably to the formation of compounds in solution. From the regularities described, it would appear that *l*-aspartic acid and *l*-asparagine possess the same relative configuration as *l*-malic acid, and that the conversion of *l*-asparagine into *l*-malic acid by nitrous acid is unaccompanied by a Walden inversion. T. S. Pa.

Photochemical Reactions in Mixtures of Ozone and Hydrogen. Fritz Weigert and Hans Böhm (*Zeitsch. physikal. Chem.*, 1915, **90**, 189—222).—Mixtures of ozone and dry hydrogen containing from 2·4% to 92·5% of hydrogen have been subjected to the light from a quartz mercury lamp which was fed by a current of 6 amperes at 65 volts. The gas was passed in a stream along a tube which was of such dimensions that it contained, in all experiments, sufficient ozone to absorb completely the whole of the photochemically active light, particularly that with wave-length about 258 $\mu\mu$. By means of these experiments the catalytic influence of ultraviolet rays on the simultaneous ozone decomposition and water formation in the mixtures was carefully studied. By measuring the volume change occasioned by illumination, and by analysis of the gas mixture before and after illumination, it was shown to be possible to determine the extent to which both changes had taken place. It is shown that when the gaseous mixture is kept in the dark no reaction of any kind takes place between ozone and hydrogen. On illumination, the two reactions I, $2O_3=3O_2$ and II, $H_2+O_3=H_2O+O_2$ occur, and, further, the reaction III, $2O_3+H_2=H_2O_2+2O_2$, cannot be observed under the experimental conditions. A consideration of the volume changes which occur on illumination shows that with a large excess of hydrogen the reaction takes place mainly according to equation II, but with larger quantities of ozone equation I represents the major portion of the reaction. Equation I is accompanied by an increase in volume, whereas equation II is accompanied by a decrease. At the point where there is neither contraction nor increase in volume, it is shown that of three molecules of ozone reacting, two react according to equation I and one according to equation II. The photochemical decomposition of ozone in the absence of hydrogen is a relatively slow process, but is strongly accelerated by even small quantities of hydrogen. With a small quantity of hydrogen, the velocity of decomposition of ozone is proportional to the ozone concentration, and from 8% hydrogen upwards it is independent of the hydrogen concentration. From

the departure of the curves from the straight line at the beginning and the end, it is shown that with large excess of hydrogen the order of the reaction is greater than unity, but with larger ozone concentrations it is less than unity. From this it is shown that the effect of two simultaneously occurring photochemical reactions cannot be regarded as the same as the sum of the two single effects. The photochemical water formation is proportional to the ozone concentration for low concentrations of ozone, but at higher concentrations of ozone it approaches a limiting value, which lies higher the higher the partial pressure of the hydrogen. With a constant ozone concentration the water formation is approximately proportional to the hydrogen concentration. With an excess of hydrogen of about one hundred times the quantity required for the formation of water according to equation II, the reaction proceeds practically entirely according to this equation. J. F. S.

Disturbances in Photochemical Gas Reactions. Fritz Weigert (*Zeitsch. physikal. Chem.*, 1915, **90**, 223—235. Compare preceding abstract).—A theoretical paper in which the various disturbing factors of photochemical gas reactions are discussed. It is shown that in relatively rapid photochemical gas reactions the shape of the containing vessel, the conditions under which the illumination is effected, diffusion, convection, and the conditions affecting the conduction of heat from the reaction vessel are determinative of the total course of the reaction. This is held to be a probable reason for the contradictory results obtained for the same reaction. Further, an apparently simple quantitative reaction may be due to the compensation of different disturbing effects. It is held that "disturbed" photochemical gas reactions are more frequent than has hitherto been held to be the case, and in all probability a revision of these reactions will lead to a new photokinetic method of representation. The disturbances are due to a too rapid course of the reaction, which causes the gas to become chemically non-homogeneous. J. F. S.

Photochemical Sensitiveness and Photoelectric Conductivity. M. Volmer (*Zeitsch. Elektrochem.*, 1915, **21**, 113—117).—The author has investigated the photoelectric conductivity of a large number of substances which are sensitive to light. It is shown that in the majority of the cases investigated a photochemical reaction and a photoelectric conductivity are induced simultaneously when the substance in question is submitted to the influence of light. The mechanism of the photoelectric conductivity is shown to consist in a loosening of electrons, which are then passed on to neighbouring molecules in much the same way as in the Grotthus theory of ionic conductivity. The theory advanced brings the two effects, photochemical sensitiveness and photoelectric conductivity, into close relationship, and confirms the Luther theory that a loosening of electrons is the immediate cause of photochemical processes. J. F. S.

Velocities of the α-Particles from Thorium Active Deposit. A. B. Wood (*Phil. Mag.*, 1915, [vi], **30**, 702—710).—A comparison has been made of the velocities of the two groups of α-particles which are expelled from thorium active deposit. The rays were deflected by a magnetic field and the radii of curvature of the paths determined by a photographic method. Assuming $1{\cdot}922 \times 10^9$ cm. per second as the velocity of the α-particles from radium-*C*, the velocity of the particles from thorium-C_1 (range 4·8 cm.) is $1{\cdot}714 \times 10^9$ and that of the particles from thorium-C_2 (range 8·6 cm.) $2{\cdot}060 \times 10^9$ cm. per second. The ratio of these velocities is 1 : 0·832, whereas Geiger's relation, $v^3 = kR$, where v is the velocity, R the range, and k a constant, gives 1 : 0·826. In view of this divergence, it is suggested that the value 4·8 cm., previously accepted as the range of the α-particles from thorium-C_1, should be increased to 4·95 cm. H. M. D.

Energy Relations Involved in the Formation of Complex Atoms. William D. Harkins and Ernest D. Wilson (*Phil. Mag.*, 1915, [vi], **30**, 723—734).—If the mass of a body is a function of the total energy as represented by Einstein's equation, $M = E/c^2$, in which M is the mass, E the energy, and c the velocity of light, the energy liberated in the formation of an atom of helium from four of hydrogen is $\Delta E = 9 \times 10^{20}(4{\cdot}00 - 4{\cdot}0312$ ergs $= 6{\cdot}708 \times 10^{11}$ cal. The formation of helium in the disintegration of the radioactive elements is considered to be connected with the much greater stability of the helium atom as compared with four hydrogen atoms which this difference in the total energy content indicates. By comparison with the above quantity, the changes in total energy associated with chemical reactions are extremely small. The heat liberated in the formation of a gram molecule of water corresponds with a change in mass of $3{\cdot}18 \times 10^{-9}$ gram, which is too small to be detected by any known method.

From the fact that 1 gram of radium in equilibrium with its products of disintegration down to radium-*C* liberates heat at the rate of 132 cal. per hour, it is calculated that the total heat liberated in the transformation of an atom of radium into radium-*C* is equal to $6{\cdot}6 \times 10^{11}$ cal. or $2{\cdot}76 \times 10^{19}$ ergs. From this the change in mass $\Delta M = 2{\cdot}76 \times 10^{19}/9 \times 10^{20} = 0{\cdot}0307$ gram. This represents the change in the mass over and above that which corresponds with the loss of the helium atom. The difference between the atomic weights of radium and lead which is due to this liberation of energy cannot be much greater than this.

The question of atomic structure is discussed, and it is shown that the atoms of the elements in the first three series of the periodic table may be represented, in most cases very closely, as combinations of helium atoms or helium atoms plus hydrogen atoms. The elements in the even-numbered groups are thus found to be built up entirely of helium nuclei. H. M. D.

Ionic Mobilities in Hydrogen. A. M. Tyndall (*Phil. Mag.*, 1915, [vi], **30**, 743—744).—Previous measurements (*ibid.*, 1910, [vi],

19, 453) of the pressure of the electric wind from a discharging point showed that this was very small in pure hydrogen. The average mobility of the negative ions deduced from these measurements was so high as to suggest that the results were spurious. It is now considered that the high average mobility is to be attributed to the occurrence of free electrons in the gas. H. M. D.

Electron Theory of the Metals and the Nernst Formula. KARL F. HERZFELD (*Physikal. Zeitsch.*, 1915, **16**, 354—362).—A theoretical paper in which the author discusses Nernst's formula for the difference of potential at the surface of contact of a metal and a solution of the corresponding ions in reference to the electron theory of the metals. Formulæ are derived which show the connexion between the difference of potential (or the polarisation) and the number of electrons in the metal. In all probability the number of such free electrons is small. H. M. D.

Reducing Power of Photographic Developers as Measured by their Single Potentials. FRANCIS C. FRARY and ADOLPH H. NIETZ (*J. Amer. Chem. Soc.*, 1915, **37**, 2246—2263).—An account is given of experiments made with the object of determining the reducing power of photographic developers by measurements of their single potentials. The theory of the single potential of a developer and the conditions which retard the attainment of equilibrium in measurements of such potentials are discussed. The absolute or relative reducing power of developers seems to be only directly determinable by the calculation of the partial pressure of hydrogen to which the developer is equivalent. The results of the experiments show that the relative reducing powers of quinol, metol-quinol, amidol, and thiocarbamide are 1·0 : 2·7 : 36·0 : 53·3. It is shown that these results appear quite reasonable from the photographic point of view. E. G.

Hydrogen Potentials of Sodium Hydroxide Solutions and the Dissociation Constant of Water. FRANCIS C. FRARY and ADOLPH H. NIETZ (*J. Amer. Chem. Soc.*, 1915, **37**, 2263—2268 .—In connexion with the authors' work on the single potential of photographic developers (preceding abstract), a knowledge of the hydrogen potential of sodium hydroxide solutions was required. Lorenz and Mohn (A., 1907, ii, 838) have made a few measurements of this constant, but their values do not cover a sufficient range. Further determinations have therefore been made at 25° with the use of a normal calomel electrode and a saturated solution of potassium chloride as the intermediate liquid. It is shown that from the results obtained the hydrogen ion concentration in sodium hydroxide solutions can be calculated from the formula E_h (the potential on the hydrogen scale) $= 0{\cdot}05909 \log 1/c'$, where c' is the hydrogen ion concentration in the sodium hydroxide solution at 25°. In order to convert these values into the corresponding concentrations of the hydroxyl ion, it is only necessary to know the dissociation constant of water, k_w, in presence of sodium

hydroxide. By means of the results of the hydrogen potential determinations, the value $1{\cdot}76 \times 10^{-14}$ was obtained for k_w at 25°.

E. G.

Hydrolysis of Sodium Carbonate in Solution. Francis C. Frary and Adolph H. Nietz (*J. Amer. Chem. Soc.*, 1915, **37**, 2268—2273).—In a study of the reactions between sodium carbonate and certain photographic developers (preceding abstracts), a knowledge of the hydrolysis constant,

$$K = [NaOH][NaHCO_3]/[Na_2CO_3],$$

was required. Experiments have therefore been carried out on the hydrolysis of sodium carbonate in solutions of various concentrations at 25°, and the results are shown to be in satisfactory agreement with those obtained by Auerbach and Pick (A., 1911, ii, 1078). Assuming the dissociation constant of water in presence of sodium hydroxide to be $1{\cdot}76 \times 10^{-14}$ at 25° (*loc. cit.*), the value of $k_4 = [HCO_3'][OH']/[CO_3'']$ is found to be 28×10^{-5}, as compared with 19×10^{-5} obtained by Auerbach and Pick. E. G.

Electromotive Forces in Alcohol. VII. Concentration Cells with Calomel Electrodes. Edgar Newbery (T., 1915, **107**, 1520—1526. Compare this vol., ii, 509).—Measurements have been made of the *E.M.F.* of concentration cells in which the potentials of mercury in the aqueous and alcoholic solutions of sodium chloride used in the previous work were directly compared with each other. The results obtained with the alcoholic solutions are in good agreement with the values calculated from Nernst's equation showing that the potential of the calomel electrode in alcoholic sodium chloride solutions varies according to the same laws which govern the variation in dilute aqueous solutions.

It is shown that the capillary electrometer gives trustworthy values for the absolute potential of mercury in concentrated aqueous and in alcoholic solutions, but that the dropping electrode can only be used with dilute aqueous solutions of certain salts. The absolute potentials of mercury in saturated solutions of sodium chloride in water and in ethyl alcohol at 25° are almost identical and equal to 0·483 volt. By making use of this value, the absolute potential of the hydrogen electrode in a $N/10$-solution of hydrochloric acid and in dry alcohol at 25° is found to be 0·299 volt.

H. M. D.

The Electromotive Force of Movement. St. Procopiu (*Compt. rend.*, 1915, **161**, 492—494).—The author has studied the production of electromotive force by the movement of an electrode, solid or liquid, in a liquid, water or an electrolyte. If the liquid in which the electrodes are placed is distilled water, an *E.M.F.* is produced, and those metals which have an osmotic pressure of solution less than that of hydrogen become negative, whilst those metals which have an osmotic pressure greater than that of hydrogen become positive. The results obtained can be expressed by the equation $e = k \log_{10} . c_1/c_2$, where $k = 0{\cdot}005$, c_1 is the osmotic

pressure of the metal, and c_2 is the osmotic pressure of hydrogen. In acids, the electromotive force of movement follows the same continuous series of the osmotic pressures of the metals, but the results do not obey quantitatively the logarithmic law given. If the cation hydrogen is replaced by potassium, using a solution of potassium hydroxide, all the metals become negative by movement. When the solution possesses the same cation as the electrode, the metal always becomes positive by movement, the metals arranging themselves according to their osmotic pressures. The concentration of the solution has no appreciable influence on the results.

W. G.

Decomposition Voltages of Molten Alkali Hydroxides. BERNHARD NEUMANN and EINAR BERGVE (*Zeitsch. Elektrochem.*, 1915, **21**, 143—152).—The decomposition voltage of molten sodium hydroxide, potassium hydroxide, sodium hydroxide to which 2% of peroxide has been added, and a molecular mixture of sodium and potassium hydroxides have been measured in the presence of air and in a nitrogen atmosphere at 180° to 640°. In the case of sodium hydroxide, it is shown that the decomposition voltage decreases from 2·38 volts at 180° to 1·32 volts at 640°. The values obtained with potassium hydroxide were lower than those obtained for sodium hydroxide at the same temperature. This fact is not in accordance with the position of the two elements in the potential series, and is explained by the absorption of oxygen with the formation of peroxide, which acts as a depolariser. When the experiments were repeated in an atmosphere of nitrogen, values were obtained which are higher than those for sodium hydroxide, and decrease from 2·4 volts at 200° to 1·8 at 550°. The temperature-coefficient for sodium hydroxide is found to be $2{\cdot}95 \times 10^{-3}$, and $3{\cdot}05 \times 10^{-3}$ for potassium hydroxide at temperatures above 335°; the value below this temperature is less, for reasons which are considered in the paper. Attempts to measure the decomposition voltage of lithium hydroxide failed to give a value for Li|LiOH, but gave figures approximating to that of the water decomposition. Several experiments were carried out with the object of determining directly the potential of sodium and potassium. The following electrolytic cells were measured: Na|NaOH(fused)|Ni; K|KOH(fused)|Ni. The value Ni|alkali being known, the values Na|NaOH and K|KOH, respectively, were calculated. Na|NaOH|Ni = 1·4 volts, whence Na|NaOH = 2·0 volts at about 320°; K|KOH|Ni = 1·76 volts, whence K|KOH = 2·36 volts at about 320°. Finally, the cell Na|NaOH(fused)|KOH(fused)|K was measured, and found to have a value fluctuating between 0·34 and 0·38 volt.

J. F. S.

Decomposition Voltages of Molten Alkali Haloids and Alkaline Earth Chlorides. BERNHARD NEUMANN and EINAR BERGVE (*Zeitsch. Elektrochem.*, 1915, **21**, 152—160).—The decomposition voltage of molten lithium chloride, sodium chloride, potassium chloride, sodium carbonate, calcium chloride, strontium

chloride, barium chloride, magnesium chloride, mixtures of sodium and potassium bromides, sodium and potassium iodides, and sodium and potassium sulphates have been determined at a series of temperatures. The measurements were carried out in carbon crucibles, using graphite electrodes. The following values were obtained: lithium chloride, 2·62 volts at 630°, temperature-coefficient $1·35 \times 10^{-3}$; sodium chloride, 2·6 volts at 835°, *t.c.* $1·46 \times 10^{-3}$; potassium chloride, 2·8 volts at 810°; *t.c.* $1·51 \times 10^{-3}$; sodium bromide, 2·45 volts at 690°, *t.c.* $1·465 \times 10^{-3}$; potassium bromide, 2·6 volts at 690°, *t.c.* $1·465 \times 10^{-3}$; sodium iodide, 2·05 volts at 630°, *t.c.* $1·48 \times 10^{-3}$; potassium iodide, 2·2 volts at 630°, *t.c.* $1·48 \times 10^{-3}$; sodium sulphate, 2·5 volts at 890°, *t.c.* $2·00 \times 10^{-3}$; potassium sulphate, 2·6 volts at 890°, *t.c.* $2·00 \times 10^{-3}$; sodium carbonate, 1·3 and 2·1 volts at 770°; calcium chloride, 2·85 volts at 585°, *t.c.* $0·685 \times 10^{-3}$; strontium chloride, 3·0 volts at 615°, *t.c.* $0·715 \times 10^{-3}$; and barium chloride, 3·05 volts at 650°. Since the decomposition voltage rapidly decreases with increasing temperature, it is deduced that the affinity between the elements vanishes at the following temperatures: LiCl, 2950°; NaCl, 2640°; KCl, 2720°; NaBr, 2440°; KBr, 2510°; NaI, 1990°; KI, 2120°; Na_2SO_4, 2000°; K_2SO_4, 2150. Using the temperature-coefficient of the decomposition voltage, and calculating the value of the decomposition voltage for 18°, and subtracting from this the values of the absolute potentials of chlorine (1·33 volts), bromine (0·993 volt), and iodine (0·53 volt) in the respective cases, it is shown that the absolute potentials of the elements lithium, sodium, and potassium are 2·03, 2·44, and 2·60 volts, respectively, at 18°. The results of the decomposition voltage determinations are considered theoretically from the second law of thermodynamics and from thermal changes. J. F. S.

Interpretation of the Labile Part of the Theoretical Isotherm. G. Bakker (*Zeitsch. physikal. Chem.*, 1915, **90**, 359—380).—A theoretical paper. Stefan and Rayleigh have assumed that the thermal or kinetic pressure has the same value for a point in a capillary layer as for a point in a homogeneous phase of the same density. Van der Waals has made a similar assumption with regard to the entropy. In the present paper, the thermal or kinetic pressure of a point in the capillary layer is given by the formula $\Theta = p + a\rho^2$, in which ρ is the density and p the pressure in the phase concerned. In this way, each point of the capillary layer corresponds with a definite homogeneous phase of the theoretical isotherm. If the mean pressure in the horizontal direction of a capillary layer is expressed by p_T and in a vertical direction by p_N, and if now the limits of capillarity are so chosen that the mean density ρ is the arithmetic mean of the densities of the limiting phases of the capillary layer ρ_1 and ρ_2, then the equation $Td\eta = d\epsilon + p_T dv$ is obtained as the energy differential equation, in which $v = 2v_1v_2/(v_1 + v_2)$ represents the specific volume of the capillary layer. Hence the energy differential equation has

the same form for a capillary layer as for a homogeneous phase. It is shown that p_T has the same value as the pressure in a homogeneous labile phase, for which the thermodynamic potential, μ, has the same value as for the homogeneous phases which bound the capillary layer. This statement is applicable to a curved capillary layer. Using the same symbols, but adding the index 3 to represent the theoretical labile phase, the equations $Td\eta = d\epsilon + p_1 dv$ and $Td\eta_3 = d\epsilon_3 + p_3 dv_3$ hold simultaneously, and $p = p_3$ and $\mu = \mu_3$. For a homogeneous phase, $(d\mu/dp)_t = v$, hence $(d\mu_3/dp_3)_t = v_3$, and consequently $(d\mu/dp_T)_t = v$. Therefore the conclusion may be drawn that $v = v_3$. A capillary layer which lies, for example, between the homogeneous phases which occur at the maximum and minimum of the theoretical isotherm, and consequently is in equilibrium with these phases, must have the same values as these phases for its pressure, density, thermodynamic potential, entropy, and all other thermodynamic quantities. This is all expressed by the statement that the capillary layer between the two homogeneous phases liquid and vapour can be regarded as representative of the labile phase, which must have the same thermodynamic potential as the capillary layer.

From this the following interpretation of the theoretical isotherm is drawn. If in the diagram of the isothermal curves for each curved capillary layer the points representing the pressure, p_T, and the specific volume are plotted, then these points give the labile portion of the theoretical isotherm. The work used in vaporisation has been resolved into four partial work quantities, two of which are connected with the metastable phase and two with the capillary layer. J. F. S.

Entropy in Condensed (Solid and Liquid) Substances and its Variations during Changes of State. Stefano Pagliani (*Nuovo Cim.*, 1915, [vi], **10**, ii, 5—33).—A large part of this paper has been already published (this vol., ii, 672). Further considerations lead to the general law that both the values of the entropy of the elements in the three states of aggregation, and also their variations on change of state, tend to diminish as the atomic coefficient increases, that is, as the number of atoms in unit of mass diminishes; this law holds for the metals and for the non-metals, taken separately. From the fact that such relation is obeyed rigorously only by the elements constituting any one group of the periodic system, the conclusion is drawn that the entropy is influenced also by the chemical character of the element. Thus, with equal atomic coefficients, the magnitude of the entropy is greater for the alkali metals than for the others, and relatively less for the non-metals than for the metals. T. H. P.

An Electrically Heated Pressure Apparatus for the Investigation of Melting Points and Transition Phenomena of Salts, Mixtures of Salts, Metals, and Alloys. Ernst Jänecke (*Zeitsch. physikal. Chem.*, 1915, **90**, 257—264).—A press is described capable of working up to pressures of 30,000 kilograms, which by means of

a lower cylinder with narrow holes bored vertically in it forces a molten solid out of the pressure chamber and so causes a sudden drop in pressure. The sudden drop in pressure is indicative of the melting of the solid. The press is heated by a chromium nickel-wound asbestos electric furnace, and the temperatures are recorded by a copper constantan thermo-element. A pendulum manometer for use with the press is described; this allows a minimum pressure of 2·4 kilograms to be read, so that its accuracy may be 1/20%. By plotting temperature and pressure readings, *PT* curves can be obtained, and consequently transition points deduced. J. F. S.

Determination of the Melting Point of $CaSO_4,2H_2O$, $BaCl_2,2H_2O$, Na_2CO_3,H_2O, $Na_2B_4O_7,5H_2O$, the Hydrates of $CuSO_4$ and Carnallite by Means of an Electrically Heated Pressure Apparatus. Ernst Jänecke (*Zeitsch. physikal. Chem.*, 1915, **90**, 265—279. Compare preceding abstract).—Using the electrically heated pressure apparatus, the author shows that gypsum melts at 107°, and is converted into the compound $CaSO_4,\frac{1}{2}H_2O$. This is proved by removing the liquid produced by pressure and weighing the solid residue, the point at which the change occurs being shown by the sudden decrease in the pressure. It is also shown that at 100° $BaCl_2,2H_2O$ melts and is converted into $BaCl_2$; Na_2CO_3,H_2O melts at 107°, and leaves anhydrous sodium carbonate; $Na_2B_4O_7,5H_2O$ melts and is converted into $Na_2B_4O_7,2H_2O$. The latter hydrate was stated to exist by Lescour (*Ann. chim. Phys.*, 1896, [vii], **9**, 543). With copper sulphates the transition points of the three well-known hydrates were obtained, and it is shown to be probable that a further hydrate, $CuSO_4,\frac{1}{2}H_2O$, also exists. Carnallite is shown to melt at 168°, and on applying further pressure to the molten salt to remove the mother liquor, pure potassium chloride remains behind. J. F. S.

Transition Points of $AgNO_3$, NH_4NO_3, and KNO_3. Ernst Jänecke (*Zeitsch. physikal. Chem.*, 1915, **90**, 280—295. Compare preceding abstracts).—The author's new pressure apparatus has been employed to determine the transition points of silver nitrate, ammonium nitrate, and potassium nitrate. Results were obtained in good agreement with those generally accepted. In the case of potassium nitrate, a second transition point is observed at about 151°, pointing to the existence of a third variety of potassium nitrate. J. F. S.

Transition Phenomena of Isomorphous Mixtures of KCl–NaCl and AgCl–NaCl, and Complete Diagrams of Condition of these Substances. Ernst Jänecke (*Zeitsch. physikal. Chem.*, 1915, **90**, 296—312. Compare preceding abstracts).—Pressure-temperature curves of the isomorphous mixtures KCl–NaCl and AgCl–NaCl have been prepared as the result of pressure experiments on these mixtures. It has been found possible in this way to prepare a complete diagram of condition. The mixtures investigated have peculiar points of interest. The binary mixture

KCl–NaCl exhibits a minimum melting point, and the mixture should theoretically exhibit "unmixing," that is, there should be separation of the pure constituents. This phenomenon has been observed in binary isomorphous mixtures, but until the present work no record has been obtained of the whole course of separation curve. In the other case, AgCl–NaCl, where no minimum melting point occurs, such separation of the component substances has never been observed. The author has been able to show that such a separation takes place, and to plot the whole course of the separation curve. Consequently, the complete condition diagrams of the two binary systems have been now obtained for the first time. J. F. S.

Transition of the Metals Tin, Zinc, Bismuth, Cadmium, Copper, Silver, Lead, and Antimony Determined by the New Electrically Heated Pressure Apparatus. Ernst Jänecke (*Zeitsch. physikal. Chem.*, 1915, **90**, 313—339. Compare preceding abstracts).—From pressure-temperature curves the author has been able to confirm the existence of allotropic forms of the metals tin, lead, bismuth, cadmium, copper, lead, and antimony, as found by Cohen and his collaborators, and in most cases the transition temperatures now found agree with the values of Cohen, although some slight differences occur. In the case of silver, for which no allotrope has hitherto been recognised, the author shows that a transition occurs at from 118—122°. This result is confirmed by the results of Hevesy and Wolff for the thermal *E.M.F.* of a silver nickel couple (A., 1910, ii, 574). J. F. S.

Application of Cryoscopy to Chemical Analysis. Maurice Drapier (*Compt. rend.*, 1915, **161**, 461—463).—For a mixture of two substances A and B, the analysis consists in taking A as the solvent and determining the lowering of the freezing point, and then preparing artificial mixtures of A and B and determining the lowering of the freezing point for each mixture. From these results by suitable successive approximations the exact proportions of A and B in the original mixture can be obtained.

Where there is a mixture of three or more substances, A, B, C . . ., the lowering of the freezing point produced by π grams in P grams of any foreign solvent not contained in the original mixture is determined. Then the freezing point of the mixture is determined and expressed as Δ', the lowering of the freezing point of A. Then if x represents the weight of A in π grams of the mixture, $x=MP(k'\Delta-k\Delta')/k(M\Delta'-100k')$, where M is the molecular weight of A, k' the cryoscopic constant of A, k the cryoscopic constant of the external solvent, Δ the observed lowering of its freezing point. If x is small as compared with P, then the formula can be simplified to $x=MP(k'\Delta-k\Delta')/100kk'$. W. G.

Method of Determining the Boiling Point of Small Quantities of Substance. Victor Arreguine (*Anal. Fis. Quim. Argentina*, 1915, **3**, 133—154).—An account of the application of the

author's method of determining the boiling point of small quantities of liquids (determination of the temperature at which the tension of the vapour of the substance equals the atmospheric pressure) to a number of organic compounds, and a theoretical discussion of the limits of accuracy of the method. A. J. W.

Ebullioscopic Behaviour of Solvents at Different Pressures. E. Beckmann and O. Liesche (*Zeitsch. physikal. Chem.*, 1915, **90**, 129—138. Compare A., 1914, ii, 622; this vol., ii, 144).—A theoretical paper in which the error which arises in ebullioscopic measurements on the introduction of the solute is discussed. It is shown that on adding the solute the height of the liquid is increased, and this, although negligible in determinations at atmospheric pressure, introduces an error in the boiling-point elevation in determinations at reduced pressures which theoretically is extremely high. Experiment, however, shows that the error never rises to the theoretical amount, and it is in consequence shown that it is not possible to apply a correction which is sufficiently trustworthy to compensate the error. A discussion of the automatic pressure regulation as effected by the author's manostat (*loc. cit.*) is entered into, and it is shown that for the range 700—200 mm. a constant pressure to 0·01 mm. is easily maintained in short experiments (20 mins.) and 0·1 mm. in long experiments (several hours); this corresponds with temperatures constant to 0·001° and 0·01° respectively. In pressure-temperature difference determinations, occasionally irregularities are observed in consequence of disturbances of the constant ebullition relationships. At low pressures, from 150—100 mm., the uncertainty of such determinations increases, on account of the considerable increase of dp/dt, and probably on account of the influence of the relatively heavy layer of vapour over the boiling liquid. J. F. S.

Thermal Analysis of Binary Mixtures. Emile Baud (*Bull. Soc. chim.*, 1915, [iv], **17**, 329—345).—The author has determined the heat of mixing of a number of binary mixtures in an endeavour to find some relationship between this value and the properties of the two constituents of the mixtures with a view of obtaining a ready means of approximately calculating the solubility of a substance A in a liquid B by means of his formula (compare A., 1912, ii, 1147). The first point examined was the variation of the heat of mixing as a function of the relative proportions of the two components mixed, using his modification of Biron's formula to calculate Δq (compare A., 1913, ii, 1025). The mixtures examined were divisible into three classes: (1) Those the mixing of which is accompanied by absorption of heat, which, within the limits of experimental error, obey the formula $\Delta q = kx(1-x)$ (*loc. cit.*). These mixtures are purely physical, and this holds good when one of the constituents is a saturated hydrocarbon or a cyclic hydrocarbon of the type C_nH_{2n}. (2) Mixtures during the making of which there is absorption of heat, but which do not obey the above

law. (3) Mixtures which give rise to a development of heat. These last two types of mixtures are accompanied by chemical phenomena, depolymerisations or combinations. The same is true of certain mixtures which give rise to absorption or development of heat according to the proportions of the two constituents. Only in the case of class (1) is it possible to arrive at any approximate idea as to the solubility of one substance in the other from their physical properties. W. G.

The Heats of Saturation of Some Alkaline Salts. ALBERT COLSON (*Compt. rend.*, 1915, **161**, 458—461).—Using the method previously described (this vol., ii, 742), the author has determined the molecular heat of formation of saturated solutions for two potassium salts and one ammonium salt. For potassium nitrate he finds the values −7145 cal. at 13·5° and −6950 cal. at 18·5°; for potassium chloride, −4082 cal. at 5·5°, −4001 cal. at 12·5°, and −3890 cal. at 17·9°. For dilute solutions of potassium chloride the heat of solution is independent of the concentration, but varies by 10% for a difference of 15° in temperature. The molecular heat of solution for saturated solutions of ammonium chloride is −3851 cal. at 14·9° and −3714 cal. at 22·3°. With dilute solutions, ammonium chloride behaves in the same way as potassium chloride.

The heats of saturation between 5° and 21° vary by at least 7%, but the variation with temperature is always less than is the case for heats of solution for dilute solutions. W. G.

A Comparative Method for Determining Vapour Densities. PHILIP BLACKMAN (T., 1915, **107**, 1500).—A short thread of mercury is introduced into a straight capillary tube of uniform bore and about 100 cm. in length. By means of a very fine capillary (about 50 cm. long), small quantities of two different liquids are introduced into the wider tube on opposite sides of the mercury thread and the ends of the tube are sealed. The tube is then heated uniformly at a temperature which is sufficiently high to vaporise the two liquids completely, and the relative volumes occupied by the two vapours are measured. If l_1 and l_2 are the lengths of the two liquid threads, s_1 and s_2 the densities of the liquids, v_1 and v_2 the volumes occupied by the vapours, and d_1 and d_2 the densities of the respective vapours, then $s_1l_1/v_1d_1 = s_2l_2/v_2d_2$, at any rate approximately, and if d_2 is known, d_1 may be calculated from this equation. Examples are given which show that the method yields satisfactory results. H. M. D.

The True Specific Volumes and the Number of Molecules in Homologous Series of Organic Compounds. W. HERZ (*Zeitsch. Elektrochem.*, 1915, **21**, 457—458. Compare this vol., ii, 682).—The author has calculated from the formula $u = D - 1/D + 2$, in which u is the volume actually occupied by the molecules and D the dielectric constant, the volume occupied by the molecules. From these figures the true specific volume s

and n the number of molecules have been calculated. The latter quantity is obtained by means of the formula $n=s/(4/3r^3\pi)$, in which the mean radius 1×10^{-8} cm. is used. By multiplying n by the molecular weight the Avogadro number is obtained. These calculations have been made for the following homologous series: aliphatic alcohols, ketones, monocarboxylic acids, esters, nitriles, primary, secondary, and tertiary amines, and aromatic amines. In every case it is shown that the u, s, D, and n values decrease with increasing molecular weight. The value of the Avogadro number varies between 60×10^{22} and 240×10^{22}. J. F. S.

Adsorption of Alcoholic Solutions by Carbon. Bror Gustafson (*Zeitsch. Elektrochem.*, 1915, **21**, 459—461).—The adsorption of phenol, benzoic acid, and picric acid from alcoholic solutions by carbon has been studied. Not only the amount of dissolved substance adsorbed by the carbon, but also the amount of solvent, are determined and used in the subsequent calculations. It is shown that there is no sign of a saturation value, as assumed by Schmidt and others; the appearance of this value is due to an erroneous method of calculation of the experimental results based on the unjustifiable assumption that the volume of the solution is constant. In the present experiments, which are only to be regarded as of a preliminary nature, it is shown that the u_0 and $u_0(1-c)$ values increase continuously to a minimum and then decrease. The adsorption of picric acid is in accordance with the Freundlich adsorption formula, even when account is taken of the amount of solvent adsorbed by the charcoal. J. F. S.

An Experiment of J. J. Thomson on the Dissociation of Iodine Vapour by the Passage of Electric Sparks. Gerhardt C. Schmidt (*Zeitsch. Elektrochem.*, 1915, **21**, 463. Compare Kropp, this vol., ii, 677).—It was shown (*loc. cit.*) that Kropp had failed to obtain the large permanent dissociation of iodine vapour obtained by Thomson when electric sparks were passed through the vapour (A., 1887, 1013). The author now draws attention to the fact that Perman (A., 1891, 453) had previously been unable to repeat Thomson's experiments. J. F. S.

Diffusion of Solutions. Mario Torre (*Anal. Fis. Quim. Argentina*, 1915, **3**, 5—11).—An investigation of the diffusion of solutions of salts of chromium, manganese, iron, nickel, and cobalt. The quantity diffused in twenty-four hours was found to be proportional to the concentration, and for similar concentrations to be proportional to the temperature. The values of the molecular diffusion, the specific diffusion constant, and the diffusion constants of Long and Beilstein are also given. A. J. W.

Preparation of Collodion Dialysers of Graded Permeability. William Brown (*Biochem. J.*, 1915, **9**, 320).—Two methods for preparing collodion dialysers, constant in character but of a wide range of permeability, are in use by the author. One consists in

steeping air-dried collodion membranes in aqueous alcohol of varying strengths, and the other in a process of differential drying (compare Walpole, this vol., ii, 549). J. C. W.

A New Form and Principle of the Dilution Law of Electrolytes. G. von Georgevics (*Zeitsch. physikal. Chem.*, 1915, **90**, 340—358).—A theoretical paper in which it is shown that there exists a series of definite relationships between the internal friction and the migration velocity of ions on the one hand, and the index n of the general dilution law formula, $c_i^n/c_s=k$, on the other. The relationships are due to the chemical affinity existing between the water and the dissolved electrolyte. This relationship does not suffice, however, to explain the different n values, and it is shown that the assumption that an attractive force exists between the ions even in the most dilute solutions, together with an absorption, with water as the absorbent, will explain the course of the n value, and that this value is determined by these two factors. This and the fact that the n value is quite independent of the number of the ions lead to the conclusion that the law of mass action does not hold when applied to ionisation in aqueous solution. This result is supported by the fact that the electrolytic n value for acids and bases approaches unity with increasing dilution. An explanation of these facts is obtained if ionisation is regarded as the result of two forces, the one holding the ions together and the other tending to separate them. The equation representing the ionisation in this case would have the simple form $c_i/c_s=k$. Since this under certain conditions actually represents the ionisation, it is necessary to assume that in these circumstances adsorption and attractive action of the ions and all other complications do not take place. It is shown that the partition of a substance between two phases is governed by an analogous formula, $c_1^n/c_2=k$, and that for this also $n=1$ if no complications enter into the reaction, so that the change of the degree of dissociation in dilute solutions is to be explained only by absorption and an ion attraction. J. F. S.

An Hypothesis on the Condition of Dissolved Electrolytes. II. H. C. S. Snethlage (*Zeitsch. physikal. Chem.*, 1915, **90**, 139—188. Compare this vol., ii, 615).—A theoretical paper in which the theory put forward in the previous paper is developed for aqueous solutions of electrolytes. It is shown that electrolytes in aqueous solution, just as in alcoholic solution, may be divided into two groups. The first group includes the strong electrolytes, such as potassium chloride, nitric acid, and sodium hydroxide. It is shown that it has been proved experimentally that many of the properties of these solutions are independent of the concentration when it is calculated in mols. Two properties, the electrical conductivity of all electrolytes and the lowering of the freezing point of salts, do not behave in the same way. The change of the quantitative expression of these properties with the concentration is best explained by the assumption that the degree of dissociation

does not change. The proportionality between these factors and the concentration only appears below certain concentrations, and the limit of concentration for similar substances appears to lie at different points for different properties. Thus, for hydrochloric acid, in connexion with sucrose inversion at 50°, the limit is at $0{\cdot}01N$; for the freezing point lowering the limit lies at $0{\cdot}2$—$0{\cdot}3N$. It is also shown that the action of electrolytes with a common ion is different in cases where the action is attributed solely to this ion. The above points are not in keeping with the view of a dissociation into ions which changes with the concentration, and all point to the properties of such electrolytes being due to the entire molecules. The additive character of different properties is also in accord with this view. In these cases the solutions behave as if the molecules are in the same condition at all concentrations provided that they are not too concentrated. The application of the law of mass action to such solutions is without meaning. It is shown that the properties of solutions of electrolytes with a common ion are dependent on that part of the molecule which is not common to the electrolytes, and that they follow the order of the potential series for these elements. In the calculation of the properties of solutions of electrolytes, the expression Δ_v/Δ_A has absolutely no meaning. Concentrated solutions are not so uniform in their behaviour, but on the whole their behaviour is in accord with the present hypothesis. In some cases the activity (catalytic and electrolytic) decreases with increasing concentration, and in others (acids and bases) it increases with concentration. The activity, however, can always be calculated by the cube-root formula. This is clear from the new hypothesis, since this formula does not take account of the shift of the equilibrium between active and inactive molecules by changes of concentration. It assumes that the change of the molecular activity is proportional to the mean distance ($a\sqrt[3]{c}$) between the dissolved particles. Three assumptions to explain this are put forward and discussed. The activity of the molecule is ascribed to an irregular partition of electric charges in the molecules. An electron (in the case of binary electrolytes) has a definite position in the atomic sphere, whereby the atom gains a polarity and becomes active. The forces active between the poles are responsible for all the properties of solutions of electrolytes. The second group of electrolytes is composed of most organic acids, and probably organic bases, ammonia, sulphuric acid, and similar substances. The properties of solutions of these substances can be calculated on the assumption that they consist of two types of molecules, the one electrically and catalytically-active, the other similar to the first kind, but to a less marked extent. The first kind are not very different from those of electrolytes of the first group, and consequently the change from one kind of molecule to the other is not to be regarded as a dissociation, but rather as an activation. Of the two types of molecules in solutions of this group of electrolytes, the name "preactive" molecules is proposed for the second type. If the electric activity of preactive molecules is not too large, the factor Λ_v/Δ_A gives an approximate

measure of the degree of activation ($\Delta_A = \Delta_\infty$). The electric activity of the preactive molecules is expressed by Δ_p, and the catalytic activity by $k_p (k_A = k_H)$. An equilibrium exists between the two types of molecules, the position of which shifts with the concentration and is determined by the activity constant. There is a gradual passage from one group of electrolytes to the other, so that the strongest electrolytes of the second group are not very different from those of the first group. The two groups are much in the same relationship to one another as a gas below the critical temperature is to the same gas above the critical temperature. The relationship between the activity (electric, catalytic) of a preactive molecule and an active molecule is a characteristic quantity which is always larger for a strong electrolyte than for a weak electrolyte. Since the electrical and catalytic activity of the active molecules of different electrolytes are alike when one and the same reaction is considered, it follows that the order of the activity constants of the active molecules is the same as that of the preactive molecules. The activity of solutions is made up of the sum of two factors; if γ is the degree of activation, then $\Delta_v = \gamma\Delta_A + (1-\gamma)\Delta_p$ and $k_v = \gamma\Delta_A + (1-\gamma)k_P$. Since the equilibrium between the two kinds of molecules is governed by the law of mass action,

$$(\Delta_r/\Delta_A - r)^2/(1-r)(1-\Delta_v/\Delta_A)v = K = (k_v/k_A - f)^2/(1-f)(1-k_v/k_A)v$$

in which $k_p/k_a = f$; $\Delta_p/\Delta_A = r$, and K is the corrected activity constant. This formula has been tested on work previously published, and shown to be in accord with fact. J. F. S.

Chemical Isomerism and Polymorphism. Giuseppe Bruni (*R. Accad. Sci. Lett. Art. Padova*, 1910, **26**, 357—360*).—The author classifies these phenomena in the following manner. Two modifications which, under all the conditions investigated, form a single independent component, are polymorphic, whereas when they behave as two independent components they are isomeric. Isomerism is of two kinds: (1) isomerism of equilibrium or tautomerism, the two modifications then undergoing reciprocal transformation within the region studied; and (2) isomerism in its stricter sense, with which such transformation does not occur. The author's first method for distinguishing between polymorphism and isomerism is based on a determination of the freezing point, and in many cases is insufficiently sensitive. Theoretically equivalent to this is the cryohydric or eutectic method, which exhibits greater sensitiveness. In general, the two modifications, whether polymorphic or isomeric, have different solubilities in a given solvent, and, consequently, different eutectic points. In the case of polymorphism, only one of such points is stable, and the addition of one of the two forms to the eutectic solution of the other cannot give points intermediate to or lower than the two eutectic points.

* A copy of this paper has been sent by Prof. Bruni, along with a letter claiming that in this communication he had anticipated N. V. Sidgwick's suggestion of a method for distinguishing tautomeric, isomeric, and polymeric from polymorphic substances (T., 1915, **107**, 672).

Such intermediate or lower points do, however, occur in cases of isomerism, and are stable for isomerism in its stricter sense and transitory at least for tautomerism. T. H. P.

Investigations on Ammonia. VII. New Determination of the Ammonia Equilibrium at Ordinary Pressure. F. Haber and Alfred Maschke (*Zeitsch. Elektrochem.*, 1915, **21**, 128—130. Compare this vol., ii, 418, 419).—A new series of determinations on the equilibrium $N_2+3H_2 \rightleftarrows 2NH_3$ have been carried out at atmospheric pressure and at temperatures from 1100° to 600°. The experiments were carried out much in the same way as was previously adopted, but without specially refined apparatus. As catalysts, iron asbestos and uranium carbide were used. The equilibrium was reached from both sides, and the reaction constant obtained agreed well with that calculated by means of the formula $\log_{10}K_p=13200/4{\cdot}571T-6{\cdot}134$, which had previously been shown to represent this equilibrium at temperatures between 560° and 975° with varying pressure. The heat of formation at constant pressure is calculated from the results of the experiments at 1000° and 600°, and shown to be 12,200; in this connexion it is to be noted that, using the value 13,200 as in the above equation, calculated values are obtained which agree with the experimental values of K_p within the limits of experimental error. J. F. S.

Two Gas Reactions. Max Trautz (*Zeitsch. Elektrochem.*, 1915, **21**, 118—122).—For the most part a theoretical paper in which it is shown that the expression

$$k=x\sqrt{T}.\pi^{\nu}\left(c/e^{i}.\,1/e^{q_0/RT}+\int dT/RT^2.\int_0^T c_v.dT\right)$$

represents the most general mass-action equation. It is shown that in all cases of reactions of the second order the constant x has a value of 10^{35} and represents a definite physical constant. Measurements of Kiss (*Magyar Chemikusok. Lápja*, 1913, Evi 7—8) on the velocity of reaction between nitric oxide and chlorine have led the author to repeat this work, and from the results he is able to show that here also, where the reaction is termolecular, the value of x is also 10^{35}. J. F. S.

The Transformations and Chemical Equilibrium of Water and Solutions of Hydrogen Peroxide Exposed to Ultraviolet Light. Albert Tian (*Thesis*, 9—154).—A full account is given of experiments which have been made to ascertain the nature of the changes which take place when pure water and dilute aqueous solutions of hydrogen peroxide are submitted to the action of ultraviolet radiation. With this object in view, measurements have been made of the rate of change of the hydrogen peroxide concentration and of the volume and composition of the gas which is evolved. The influence of dissolved oxygen on these changes was also examined. Some of the results obtained have been already described in previous papers (A., 1911, ii, 35, 452, 564).

For the estimation of small quantities of hydrogen peroxide, a method has been worked out in which a slight excess of a dilute standard solution of potassium permanganate ($N/1000$ or $N/2000$) is added to the solution under examination, together with manganous sulphate as catalyst, and the unchanged permanganate is then estimated colorimetrically. By this method $0{\cdot}85 \times 10^{-6}$ gram of hydrogen peroxide may be detected in 50 c.c. of solution. The sensitiveness of the method is consequently of the same order as that in which titanic acid is employed.

With reference to the photochemical decomposition of hydrogen peroxide in dilute aqueous solution, it has been found that the velocity increases with increasing frequency of the exciting radiation. The reaction takes place in accordance with the equation for unimolecular reactions, and when thin layers of solution of varying concentrations are exposed to the light emitted by a quartz-mercury arc lamp, the velocity is proportional to the intensity of the incident radiation and not to the absorbed luminous energy. This result is attributed to the heterogeneity of the radiation and the fact that rays of different wave-length are not absorbed in a constant ratio. The temperature-coefficient for the interval 10—30° is 1·15. The velocity is slightly diminished by the addition of small quantities of acids and very considerably increased in presence of traces of alkali. There is, however, no obvious connexion between the velocity and the concentration of the alkali as measured by the electrical conductivity of the solutions. The reaction between hydrogen peroxide and ozone is accelerated by the action of ultraviolet radiation.

Whereas ultraviolet rays of moderately short wave-length (λ 2500—3000) are able to bring about the decomposition of hydrogen peroxide at a measurable rate, pure water is only decomposed by rays in the extreme ultraviolet ($\lambda < 1900$). When such rays are present in the incident light, the water is decomposed in accordance with the reversible equation $2H_2O = H_2O_2 + 2H$ and hydrogen is set free. The hydrogen peroxide is subsequently decomposed according to the equation $H_2O_2 \longrightarrow H_2O + O$. After the lapse of a sufficient interval of time, the hydrogen and oxygen thus set free are given off in proportions which correspond very closely with those which would be obtained if the water were directly decomposed into its elements.

If the water under investigation contains dissolved oxygen, this reacts with the hydrogen set free in the primary photochemical decomposition of the water, and thus indirectly increases the rate of formation of hydrogen peroxide in that the velocity of the reversed reaction $H_2O_2 + 2H \longrightarrow 2H_2O$ is thereby diminished. At the same time, the dissolved oxygen is to some extent transformed into ozone under the influence of the ultra-violet rays, and the ozone formed reacts with the hydrogen peroxide. Special experiments have shown that ozone has no action on water under these conditions.

In consequence of the above-mentioned secondary reactions, the rate at which hydrogen peroxide is formed varies considerably with

the conditions of the experiment. These changes have also an influence on the limiting concentration of the hydrogen peroxide which is attained when the water has been exposed to the ultraviolet rays for a sufficient length of time.

The observations show that conditions favourable to the formation of hydrogen peroxide are obtained (1) by the use of a source of ultraviolet light which is rich in rays of very short wave-length; (2) by exposing the water to the action of the light in thin layers; (3) by eliminating as far as possible the factors which tend to bring about the decomposition of the hydrogen peroxide. This decomposition may be diminished by the use of pure water and of ultraviolet radiation from which the rays of moderate wave-length have been cut off. The disturbing influence of ozone may be eliminated to a large extent by passing a current of air through the solution.

In agreement with previous observations, it has been found that the radiation from high-tension quartz-mercury lamps which have been in use for some time is not nearly so rich in short-wave rays as the light which is emitted by new lamps of this type or that which is obtained from low-tension lamps.

In a general discussion of the relation between the velocity of photochemical reactions and the energy of the exciting radiation, it is shown that the frequently assumed proportionality between the velocity and the quantity of absorbed monochromatic radiation is only to be expected when the photochemical activity and the absorption constant vary in such a way that the ratio of these quantities remains constant. If the reaction is of the first order and Beer's law expresses the absorption, this condition is satisfied and proportionality between the desired effect and the absorbed energy may be anticipated. The same relation must obtain for the rays of different frequency if the exciting light is not homogeneous.

H. M. D.

The Dual Theory of Acid Catalysis. Catalytic Activity of Monochloroacetic Acid in Presence of its Salts. HARRY MEDFORTH DAWSON and CLARENCE KENWORTHY REIMAN (T., 1915, **107**, 1426—1437).—According to Arrhenius's experiments (*Zeitsch. physikal. Chem.*, 1890, **5**, 1) on the velocity of inversion of sucrose under the catalytic influence of acetic and formic acids in presence of the corresponding salts, it would appear that the reduction in the activity of the acid on the addition of salt is proportional to the diminution in the hydrogen ion concentration. These results seem to show that the catalytic activity of an acid is determined solely by the concentration of the hydrogen ions in the solution. They are incompatible with the view that the acid exerts a catalytic influence both in the ionised and non-ionised condition. According to Arrhenius, the velocity of the inversion of sucrose by $0{\cdot}25N$ acetic acid is reduced to about one-seventieth by the addition of $0{\cdot}25N$ sodium acetate. Assuming a dual catalytic effect and making use of the velocity coefficients derived from observations on the rate of isomeric change of acetone in presence of

acetic acid, it can be shown that the catalytic activity of $0{\cdot}25N$ acetic acid should not fall below about 28% of the velocity for the free acid, even when the sodium salt is added in such quantity as to reduce the ionisation to a negligibly small quantity.

In view of this discrepancy and to test the requirements of the dual theory of catalysis in its application to solutions containing salts of the catalysing acid, experiments have been made on the rate of isomeric change of acetone with monochloroacetic acid as catalyst.

Two series of experiments were made with $0{\cdot}05N$ and $0{\cdot}10N$ acid to which varying quantities of the sodium salt were added. The observed velocities are in very good agreement with the values calculated from the equation $v = k_{\mathrm{H}}c\alpha + k_{\mathrm{M}}c(1-\alpha)$, in which k_{H} and k_{M} are the velocity coefficients for hydrogen ion and the non-ionised acid, respectively, c is the concentration of the acid, and α its degree of ionisation. The values used for k_{H} and k_{M} are those derived from experiments with the free acid at varying concentrations. The values of α for solutions containing both acid and salt have been calculated from the mass-action equation on the assumption that the "ionisation constant" of the acid is not affected by the presence of the salt. This would seem to be justified by the measurements made by Walpole (T., 1914, **105**, 2501, 2521) of the hydrogen ion concentration in mixtures of acetic acid and sodium acetate.

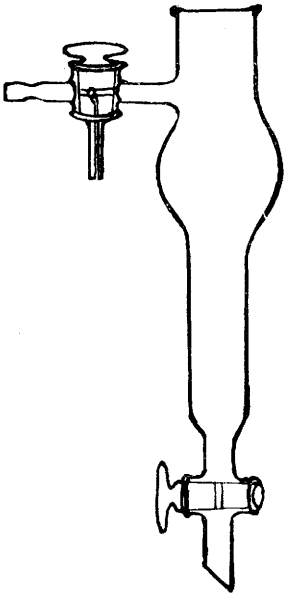
The results obtained in the experiments are unequivocally in favour of the theory of dual catalytic action as opposed to the simple hydrogen ion theory. Whether the difference between these and the results obtained by Arrhenius are due to the difference in the nature of the reactions employed is a question which cannot as yet be definitely settled, but the general body of evidence furnished by the results of the systematic investigation of acids is not favourable to such a view. H. M. D.

A New Micro-balance. E. H. Riesenfeld and H. F. Möller (*Zeitsch. Elektrochem.*, 1915, **21**, 131—136).—After a description of the various forms of micro-balances which have been put forward, the authors describe a new form, which they claim to be sensitive to $3{\cdot}3 \times 10^{-8}$ gram with a maximum load of 5 mg. The balance consists of a glass capillary tube as arm, which is fastened to a quartz thread supported by a brass fork. The arm is 13 cm. long, and is supported and fastened to the quartz thread at a point 3 cm. from one end. At the shorter end a small silver mirror, made from a quarter of a microscope cover glass, is attached, and at the other the pan. A number of different methods of supporting the pan are described, the most successful for high sensitiveness being a quartz thread fastened at right angles to the end of the arm. To this a second quartz thread is hung, and the pan attached directly to the second thread. A method of arresting the balance is also described. This consists in clamping the arm at the pan end between two feathers. Methods of using,

calibrating, and controlling the balance are described at length in the paper. J. F. S.

The Inertoid. An Automatic Apparatus for Chemical Operations in an Inert Atmosphere. Rodolfo Fritsch (*Chem. Zeit.*, 1915, **39**, 743).—A form of apparatus is described which the author has employed in chemical operations involving the use of reagents which are acted on by air or moisture. The apparatus is devoid of any novelty to which attention need be directed. H. M. D.

A Simple Apparatus for Filtration under Diminished Pressure. James Colquhoun Irvine (*Biochem. J.*, 1915, **9**, 321—322).—The tube which is shown in the accompanying figure has been designed for use with a filtering funnel or a Gooch crucible. It has many advantages, among which may be emphasised that small volumes of filtrates may be recovered without much loss, and washings may easily be removed for testing. The bulb prevents loss by frothing, and the three-way tap makes it unnecessary to stop the pump when emptying the tube. For analytical work, a tube which holds about 150 c.c. is most suitable. J. C. W.



Separating Apparatus. L. Bertiaux (*Ann. Chim. anal.*, 1915, **20**, 213—214).—The apparatus has the form of a double separating funnel, one container being placed above the other, and the two connected by a short tapped tube; taps are also provided at the upper and lower ends. After a liquid has been shaken with an immiscible solvent in the upper container and the mixture allowed to separate, the bottom layer is drawn off into the lower container, the air having been exhausted previously from the latter through a tapped side-tube. Each container is provided with a cold-water jacket, and the whole apparatus is suitably mounted on a stand. W. P. S.

Lecture Experiments for Demonstrating a Case where the Velocity of Reaction Decreases with Increase of Temperature. Anton Skrabal (*Zeitsch. Elektrochem.*, 1915, **21**, 461—463).—As the result of experiments on the Landolt reaction between iodate and sulphite, the author has found that if the reaction is allowed to take place in the presence of an excess of sulphate the velocity of the first stage is decreased so that the temperature-coefficient becomes less than unity, whereas it was previously greater than

unity. Consequently, the Landolt reaction has a temperature-coefficient greater than unity, and the velocity will increase with increase of temperature; but the reaction mixture to which sodium sulphate is added has a temperature-coefficient less than unity, and the velocity therefore decreases with increase of temperature. The experimental conditions are given for exhibiting both processes as lecture experiments.

(*a*) Temperature-coefficient greater than unity. Two solutions are made up: (i) 30 c.c. 0·01*N* HIO_3 is made up to 100 c.c., and (ii) 30 c.c. 0·01*M* $NaHSO_4$ + 10 c.c. starch solution is made up to 100 c.c. with distilled water. The two solutions are poured simultaneously into a flask, well mixed, and divided into approximately equal parts in two flasks. One flask is placed in water at 30° and the other in water at about 12°. The hot reaction sets in, as shown by the blue colour, in five minutes, the cold reaction about two minutes later.

(*b*) Temperature-coefficient less than unity. Two solutions are made up: (i) 10 c.c. of 0·01 N-HIO_3 are made up to 100 c.c. with 2*N* solution of sodium sulphate, and (ii) 10 c.c. of 0·01*M* $NaHSO_4$ + 5 c.c. 0·5*N* KI + 10 c.c. starch solution are made up to 100 c.c. with 2*N* solution of sodium sulphate. The two solutions are mixed and divided as in the last case; the one is placed in water at 30° and the other in water at 12°. The cold solution becomes blue in about fifteen minutes, and the other several minutes later. It is to be noted that the cold solution is supersaturated with regard to Glauber's salt, but generally there is no crystallisation during the experiment. J. F. S.

Inorganic Chemistry.

The Density of Argon. H. Schultze (*Ann. Physik.*, 1915, [iv] **48**, 269—272).—Measurements of the density of argon, which according to spectroscopic tests was quite pure, gave a mean value of 0·00178376 gram for the weight of 1 c.c. at 0° and 760 mm. By making use of the compressibility coefficient found in a previous investigation, the ratio of the molecular weight of argon to that of oxygen under zero pressure is derived. This number gives 39·945 for the atomic weight of argon, as compared with 39·91 found by Ramsay and Travers and 39·88 by Watson. H. M. D.

Alkali Hypochlorites as Disinfectants. Pierre Breteau (*J. Pharm. Chim.*, 1915, [vii], **12**, 248—249).—When an alkali hypochlorite solution is diluted with a large volume of water there is loss of available chlorine; for instance, the loss amounts to 3·8% if 5 c.c. of a solution containing 0·047 gram of available chlorine are diluted with 200 c.c. of water. The loss is increased by the presence of carbonates, hydrogen carbonates, or chlorides in the water. The residual hypochlorite is at the same time dissociated

to the extent of 60%, but the dissociation is diminished considerably by the presence of sodium carbonate. The addition of boric acid, with or without the subsequent addition of sodium hydrogen carbonate, to an alkali hypochlorite solution containing an excess of sodium carbonate appears to increase the disinfecting power of the solution. W. P. S.

The Preparation of Alkali Nitrates Starting from Calcium Nitrate. H. Le Chatelier and B. Bogitch (*Compt. rend.*, 1915, **161**, 475—479).—In order to overcome the difficulty of filtering the pasty precipitate of finely divided calcium sulphate obtained by the interaction of calcium nitrate and ammonium sulphate at the ordinary temperature, the two salts should be dissolved in their own weight of water and mixed in equimolecular proportions and the mixture heated at 150° in a closed vessel, when the calcium sulphate is obtained in a sandy, crystalline mass, easy to wash by decantation with hot water, and from which practically the whole of the ammonium nitrate can be obtained free from calcium sulphate in two washings. This method can be used on an industrial scale. W. G.

Potassium Ammonobariate, Ammonostrontiate, and Ammonocalciate. Edward C. Franklin (*J. Amer. Chem. Soc.*, 1915, **37**, 2295—2301).—The author has shown (A., 1907, ii, 768; 1913, ii, 956) that potassium ammonozincate and ammonomagnesiate can be prepared by the action of potassamide on zinc amide and magnesium amide, respectively, in liquid ammonia solution. It has now been found that when a barium salt and excess of potassamide are allowed to interact in liquid ammonia solution, a white, insoluble precipitate of *potassium ammonobariate*, $BaNK,2NH_3$ or $Ba(NH_2)_2,KNH_2$, is produced. *Potassium ammonostrontiate* and *ammonocalciate* have been prepared in a similar manner. E. G.

The Dissociation of Calcium Carbonate Below 500°. R. B. Sosman, J. C. Hostetter, and H. E. Merwin (*J. Washington Acad. Sci.*, 1915, **5**, 563—569).—The crystalline forms of calcium carbonate dissociate very slowly below 400°. At this temperature the dissociation pressures are of the order of 0·003 to 0·009 mm. At 425°, arragonite is transformed into calcite within an hour when a vacuum furnace is employed for the heating of the substance.

There is evidence of the existence of two forms of calcium oxide. The oxide obtained by heating calcite at a low red heat is fine-grained and porous, and shows a slight double refraction. When heated at higher temperatures, the refractive index increases and cubic, crystalline calcium oxide is formed, for which $n_D=1·83$. This cubic form is obtained directly from fused calcium nitrate, and is found in the products formed on cooling certain fused mixtures of lime, alumina, and silica. Heating curves afford evidence of a transition point between 400° and 430°. The porous form of

lime combines readily with dry carbon dioxide, the crystalline form very slowly. H. M. D.

Preparation of Metallic Strontium. MAX TRAUTZ (*Zeitsch. Elektrochem.*, 1915, **21**, 130—131).—Polemical. The author criticises certain statements of Neumann and Bergve (A., 1914, ii, 365) made in connexion with Trautz and Schrader's method of preparing strontium (*Verh. Deut. Naturf. u. Aertze*, 1911, **83**, II, 1, 196). J. F. S.

Dithiotrimercuric Double Salts. G. DENIGÈS (*Bull. Soc. chim.*, 1915, [iv], **17**, 353—359).—The author has prepared a number of crystalline salts of the type $2HgS,HgX_2$ or 2HgS,HgX, according as X is the negative ion of a monobasic or dibasic acid, by heating the original salt, HgX_2 or HgX, in dilute aqueous solution with a small amount of carbon disulphide. Thus, when mercuric sulphate (14 grams) is heated on a water-bath for half an hour with 450 c.c. of water containing 1·5 c.c. of carbon disulphide, the mixture allowed to cool, well shaken and re-heated for half an hour, and again allowed to cool, filtered, and the crystalline precipitate dried over sulphuric acid in the dark, small prisms or lozenge-shaped needles of *dithiotrimercuric sulphate*, $HgSO_4,2HgS$, are obtained which are stable even at 130°. The *nitrate*, $Hg(NO_3)_2,2HgS$, hexagonal plates; the *chloride*, $HgCl_2,2HgS$, grouped crystals resembling the backbone of a fish; the *bromide*, $HgBr_2,2HgS$, grouped needles, are similarly prepared. By dissolving 5 grams of mercuric oxide in 40 c.c. of acetic acid and 200 c.c. of water and warming the mixture with 1 c.c. of carbon disulphide as described, the *acetate*, $Hg(OAc)_2,2HgS$, was obtained as voluminous prisms. The *propionate*, $Hg(C_3H_3O_2)_2,2HgS$, more elongated prisms, were similarly prepared. All these compounds are decomposed by aqua regia, giving mercuric sulphate and the chloride, bromide, etc., as the case may be. With alkali hydroxides they are decomposed, giving the oxysulphide.

Attempts were made to use carbon oxysulphide and *iso*thiocyanic acid to prepare compounds of the types

$$Hg\begin{<}S\cdot HgA\\O\cdot HgA\end{} \qquad Hg\begin{<}S\cdot HgA\\NH\cdot HgA'\end{}$$

but in each case the product of the reaction was a simple dithiotrimercuric compound,

$$3HgA_2 + 2COS + 2H_2O = HgA_2,2HgS + 4HA + 2CO_2.$$

W. G.

Preparation of Chloroplatinic Acid, and of the Chlorides of Gold and Palladium. ENRIQUE V. ZAPPI (*Anal. Fis. Quim. Argentina*, 1915, **3**, 68—69).—As a solvent for platinum, gold, and palladium, the author recommends a mixture of concentrated hydrochloric acid and chloric acid, chlorine being generated in accordance with the equation $5HCl + HClO_3 = 3Cl_2 + 3H_2O$.

A. J. W.

Preparation of Potassium Platinochloride. ENRIQUE V. ZAPPI (*Anal. Fis. Quim. Argentina*, 1915, **3**, 186—188).—Potassium platinochloride can be prepared by the action of potassium oxalate on potassium platinichloride, the reaction corresponding with the equation $K_2PtCl_6 + C_2O_4K_2 = K_2PtCl_4 + 2KCl + CO_2$. A. J. W.

Mineralogical Chemistry.

Prehnite from Helsingfors, Finland. AARNE LAITAKARI (*Jahrb. Min.*, 1915, ii, Ref. 148; from *Geol. För. Förh.*, 1914, **36**, 432—440).—The mineral forms veins intersecting amphibole rocks in the town; associated minerals in the veins are quartz, albite, calcite, steatite, and epidote. Crystallographic and optical determinations are given; D 2·918; analysis:

SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	Na_2O.	H_2O.	Total.
43·91	23·80	0·95	0·09	26·83	trace	4·31	99·89

L. J. S.

Chemical Composition of the Scapolites. L. H. BORGSTRÖM (*Jahrb. Min.*, 1915, ii, Ref. 140—143, 143—144, 144—145; from *Zeitsch. Kryst. Min.*, 1914, **54**, 238—260, *Teknikern, Helsingfors*, 1914, and *Bull. Comm. Géol. Finlande*, 1914, No. 41).—Analyses of Finnish scapolites show an excess of bases over silica to that required by the usually accepted formula, whilst at the same time carbon dioxide is present as an essential constituent. Although calcite is frequently present as a mechanical admixture, this does not account for all the carbon dioxide. The powdered mineral effervesces only slightly in dilute hydrochloric acid, but briskly, with complete decomposition, in a mixture of hydrochloric and hydrofluoric acids. Further, there is a close connexion between the amount of carbon dioxide and the optical constants, as shown in the following table (for sodium light):

Locality.	CO_2%.	ω.	ϵ.	$\omega - \epsilon$.
I. Ersby, Pargas, Finland	4·74	1·5954	1·5569	0·0385
II. Monte Somma, Vesuvius ...	4·07	1·6066	1·5711	0·0355
III. Stillböle, Finland	3·78	1·5865	1·5585	0·0280
IV. Stansvik, Finland...	3·21	1.5841	1·5543	0·0298
V. Laurinkari, Finland	3·12	1.5804	1·5529	0.0275
VI. Haliburton, Ontario	1·59	1·5694	1·5500	0·0194
VII. Enterprise, Ontario	1·33	1·5502	1·5424	0·0178

Complete analyses of these materials gave (under the corresponding numbers):

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	Cl.	SO_3.	CO_2.	H_2O.	Total.
I.	44·45	28·06	0·44	17·72	0·31	2.71	0·29	0·03	0·00	4·74	0·85	99·60
II.	41·55	30·91	0·06	20·44	0·15	1·95	0·34	0·22	0·27	4·07	0·63	100·59
V.	46·25	26·50	0·13	16·03	0·17	3·96	0·57	0·72	1·41	3·12	1·16	100·02
VI.	51·63	24·21	0·20	11·13	0·08	7·02	0·90	2·32	0·98	1·59	0·60	100·66
VII.	54·04	21·12	0·25	8·48	2·37	7·71	0·72	2·29	0·23	1·33	1·48	100·02

To account for these variations in composition, the following five compounds are assumed; the calculated percentages of each of these present in the minerals analysed are appended:

	I.	II.	V.	VI.	VII.
Marialite (or chloride-marialite), $NaCl,3NaAlSi_3O_8$	—	8	17	53	60
Sulphate-marialite, $Na_2SO_4,3NaAlSi_3O_8$	—	4	17	—	3
Carbonate-marialite, $Na_2CO_3,3NaAlSi_3O_8$	25	—	—	—	—
Carbonate-meionite, $CaCO_3,3CaAl_2Si_2O_8$	75	88	66	35	37
Sulphate-meionite, $CaSO_4,3CaAl_2Si_2O_8$	—	—	—	12	—

The marialite molecule, $NaCl,3NaAlSi_3O_8$, is identical with that assumed by Tschermak (1883), whilst the carbonate-meionite, $CaCO_3,3CaAl_2Si_2O_8$, takes the place of his molecule, $Ca_4Al_6Si_6O_{25}$ (or $CaO,3CaAl_2Si_2O_8$, the existence of an oxide-meionite being doubted).

The groups $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$ suggest a similarity between the scapolite and the felspar groups. The specific gravity determined graphically for the pure compounds is for marialite 2·560 and for carbonate-meionite 2·772, and the corresponding molecular volumes are 331·2 and 338·2, respectively. The close agreement of the latter corresponds with the agreement in the crystal-angles and the perfect isomorphous miscibility of the series.

The third paper deals more particularly with the scapolite from Laurinkari, a small island 5 km. S.W. of Åbo, where, in association with orthite, sphene, hornblende, quartz, etc., it forms true veins in granite. D 2·698—2·719; $a:c=1:0·440$. L. J. S.

Iron Calcium Silicates: the System $FeSiO_3$—$CaSiO_3$. N. Konstantinov and B. Selivanov (*Jahrb. Min.*, 1915, ii, Ref. 145; from *Ann. Inst. Polyt. St. Petersbourg, Sect. math. phys. sc. nat.*, 1912, **17**, 427—445).—The cooling curve for $FeSiO_3$ shows a distinct break at 1145—1160°. With the addition of 25 mol. % $CaSiO_3$ the melting point reaches a minimum (1030°), the structure being eutectic. The addition of 25—65 mol. % $CaSiO_3$ gives two components with a radiating, crystalline structure. With 65 mol. % $CaSiO_3$ the melting point is 1200°, with a break in the curve. Solid solution of $CaSiO_3$ now takes place, with the separation of new crystals. The melting point of $CaSiO_3$ (pseudo-wollastonite) is 1510°. L. J. S.

Analytical Chemistry.

Nephelometry (Photometric Analysis). I. History of Method and Development of Instruments. PHILIP ADOLPH KOBER and SARA STOWELL GRAVES (*J. Ind. Eng. Chem.*, 1915, **7**, 843—847).—Mulder, in 1859, compared opalescent silver chloride suspensions obtained in filtrates from atomic weight determinations, and Stas, in 1874, used the same method for estimating the

quantity of precipitate in opalescent solutions; both these observers made their measurements on the amount of light absorbed. Richards and Wells have described an apparatus (A., 1904, ii, 287) in which the light reflected by the precipitates is measured. The authors have now devised an instrument which is built on the lines of a Duboscq colorimeter; the optical arrangement gives a Lummer-Brodhun field which increases the sensitiveness of the readings. The quantity of substance in the solution under examination should not exceed 0·1 gram per litre; 1 part of substance in 500,000 parts of liquid can be estimated by the method. Highly coloured precipitates which remain in suspension should be estimated colorimetrically, and the nephelometric method used only for colourless, colloidal suspensions. W. P. S.

The So-called Beilstein's Copper Oxide Reaction for the Detection of Halogens in Organic Substances. II. The Pyrochemical Formation of Green Copper Camphorate as a Means of Identifying Camphoric Acid. HERMANN KUNZ-KRAUSE. (*Chem. Zentr.*, 1915, ii, 49; from *Apoth. Zeit.*, 1915, **30**, 141—142). —The use of copper oxide instead of copper gauze is recommended in this test. A piece of copper oxide is heated in the outer Bunsen flame until it ceases to give a green coloration to the latter, then cooled, a small quantity of the substance to be tested is placed on the copper oxide, and this is again placed in the flame. The reaction is not always characteristic; for instance, copper benzoate and copper formate both yield a green flame with the test, although they may be free from chlorine or other halogen. Natural camphor and artificial camphor free from chlorine do not give a reaction when heated on copper oxide, but a green flame is obtained if copper gauze is used.

Camphoric acid does not yield a volatile copper compound, but if a heated piece of copper oxide is rubbed into a quantity of camphoric acid contained in a porcelain crucible lid, bright green particles appear and adhere to the porcelain. This reaction is due to the pyrogenic formation of copper camphorate. Terpene hydrate yields an odour of benzaldehyde when heated in copper oxide, but does not give a green flame reaction. W. P. S.

Detection of Iodine in Urine, Saliva, and Other Body Fluids. J. SCHUMACHER (*Chem. Zentr.*, 1915, i, 1340; from *Deut. med. Woch.*, 1915, **41**, 196—197).—Five drops of the fluid under examination are placed on a tablet of ammonium persulphate which is supported on a piece of filter-paper. If iodine is present, the portion of the paper under the tablet is coloured deep blue, or violet when only a small quantity of iodine is in the fluid. The test fails in certain cases where the iodine is in organic combination.

W. P. S.

Test for Iodine (in Urine). J. SCHUMACHER (*Chem. Zentr.*, 1915, ii, 202; from *Deut. med. Woch.*, 1915, **41**, 532).—A quantity of the urine is mixed in a test-tube with its own volume of hydrogen

peroxide solution and one-fifth of its volume of 1% benzidine solution (in alcohol); the upper part of the mixture is then heated to boiling. If iodine is present, a brown or black coloration develops; with large quantities of iodine a brown or black precipitate is obtained. The presence of very small amounts of iodine may be detected by shaking the heated mixture with a few c.c. of chloroform, in which the coloured substance is soluble. W. P. S.

Estimation of Total Sulphur in Caoutchouc Materials. A. HUTIN (*Ann. Chim. anal.*, 1915, **20**, 214—216).—From 1 to 2 grams of the coarsely divided sample are placed in a crucible and 30 c.c. of fuming nitric acid are added in small quantities at a time, the crucible being covered with an inverted funnel. When all the acid has been added, the inside of the funnel is wiped with a few small pieces of filter-paper, which are added to the crucible, the contents of the latter are evaporated to a syrupy consistence, and this residue is rendered slightly alkaline by the gradual addition of sodium hydroxide solution. A quantity of magnesium oxide sufficient to form the whole into a thick paste is now added, the mixture is dried at 140°, and incinerated. Care must be taken to apply the heat slowly, so as to prevent explosion. The ignited residue is then extracted with boiling water, the solution filtered, and the sulphuric acid precipitated as barium sulphate in the usual way. W. P. S.

Micro-reactions of Carbon Disulphide. G. DENIGES (*Bull. Soc. chim.*, 1915, [iv], **17**, 359—360).—Carbon disulphide, in minute quantities can be detected by preparing one or other of the dithiotrimercuric salts (this vol., ii, 835) and examining the crystals under a microscope. Ten c.c. of the solution of a mercuric salt is used for the preparation. W. G.

Estimation of Selenium in Sulphur. W. SMITH (*J. Ind. Eng. Chem.*, 1915, **7**, 849—850).—The method proposed depends on the decomposition of sulphur and selenium bromides by water according to the equations $2S_2Br_2 + 3H_2O = H_2SO_3 + 3S + 4HBr$ and $SeBr_4 + 3H_2O = H_2SeO_3 + 4HBr$, and on the fact that the selenium compound decomposes very rapidly as compared with the sulphur compound. When the selenium acids (small amounts of selenic acid are formed by oxidation) are heated with an excess of hydriodic acid they are reduced to selenium, $H_2SeO_4 + 6HI = 4H_2O + 3I_2 + Se$ and $H_2SeO_3 + 4HI = 3H_2O + 2I_2 + Se$. Fifty grams of the powdered sulphur are mixed with about 55 c.c. of bromine, and after fifteen minutes the mixture is shaken for one minute with 40 c.c. of bromine water, the aqueous solution separated and filtered, and the sulphur bromide extracted with four further quantities of 40 c.c. of bromine water, 2 c.c. of bromine being also added each time. The last extract is heated with hydrochloric acid and potassium iodide; if selenium is still present, the extraction with bromine water is continued. The united extracts are now boiled, treated with potassium sulphite to remove bromine

diluted to about 250 c.c., 15 c.c. of hydrochloric acid and 5 grams of potassium iodide are added, the mixture is boiled, liberated iodine is removed by the addition of potassium sulphite solution, and after twenty minutes' boiling the selenium is collected, dried at 100°, and weighed. Tellurium, if present in the sulphur, is estimated with the selenium, and may be separated by the method described by Browning and Flint (A., 1909, ii, 934). W. P. S.

Estimation of Nitrates in Soil. R. S. Potter and R. S. Snyder (*J. Ind. Eng. Chem.*, 1915, **7**, 863—864).—The use of calcium carbonate as a clarifying agent in preparing soil extracts for nitrate estimations is preferable to that of calcium oxide; low results are always obtained when calcium oxide is employed, and the deficiency is greater when the nitrate is estimated by the phenolsulphonic acid method (A., 1911, ii, 331) than it is with the reduction (aluminium) method. W. P. S.

Detection and Estimation of Very Small Quantities of Phosphoric Acid, Especially in Potable Waters. P. Medinger (*Chem. Zeit.*, 1915, **39**, 781—782).—The reagent employed is prepared as follows. Forty grams of ammonium molybdate are dissolved in 100 c.c. of water and saturated strychnine nitrate solution is added gradually until the precipitate which first forms no longer dissolves when the mixture is shaken; about 80 c.c. of the strychnine nitrate solution are required. The mixture is then poured into an equal volume (about 180 c.c.) of nitric acid (D 1·4), and after eighteen hours the solution is filtered. To detect the presence of phosphoric acid in water, twenty drops of the reagent are placed in a test-tube, 10 c.c. of the water are added, and the mixture is shaken. If the water contains as little as 0·25 mg. of P_2O_5 per litre, a turbidity develops within twenty seconds; with 2·5 mg. per litre, the turbidity appears at once, and a precipitate forms in about twenty seconds. The ordinary salts present in drinking water do not interfere, but may give a turbidity after twenty seconds. The reaction may be obtained with 1 c.c. of a water containing 0·1 mg. of P_2O_5 per litre. The sensitiveness of the reagent decreases slightly after a few days, but may be restored by the addition of a few drops of strychnine nitrate solution. The test may be applied to liquids other than water, for instance, to wine, and the quantity of phosphoric acid present estimated approximately by comparing the turbidity obtained with that produced under similar conditions by a standard phosphoric acid solution. W. P. S.

Estimation of Small Quantities of Arsenic. Lydia Bulyghin [and von Billeter] (*Chem. Zentr.*, 1915, i, 1341—1342; from *Bul. Soc. Stiinte. Bucuresti*, 1914, **23**, 195—230).—Small quantities of arsenic in organic substances are estimated by destroying the latter in the usual way, distilling the resulting solution according to the directions given by Jannasch (A., 1910, ii, 546), decomposing the hydrochloric acid in the distillate with hypochlorous

acid, and then transferring the solution to a Marsh apparatus. The zinc used in the Marsh apparatus is treated previously with copper sulphate or is coated with platinum black. The following amounts of arsenious oxide were found in various quantities of animal substances: calf's liver (50 grams), 0·0038 mg.; hair (10 grams), 0·003 mg.; nails (0·981 gram), 0·004 mg.; human liver (50 grams), 0·003 mg. W. P. S.

Micro-electro-analysis. E. H. Riesenfeld and H. F. Möller (*Zeitsch. Elektrochem.*, 1915, **21**, 137—143).—The conditions under which micro-electroanalysis may be effected have been the subject of a considerable number of experiments. All weighings in connexion with the work were made on the micro-balance previously described (this vol., ii, 831). It is shown that ordinary laboratory reagents are not sufficiently pure for this work and must be specially purified. Sulphuric acid, for example, on electrolysis deposits lead on the cathode; a 2*N* solution deposited 48·9 μ grams from 20 c.c. of the solution, but when purified by distillation the same volume yielded only 0·6 μ gram. It is further shown that platinum dissolves from the anode in amounts which, whilst being quite negligible in ordinary work, are extremely large in micro-work. Thus 1 gram of the purest potassium cyanide in 30 c.c. of water, when electrolysed with a platinum wire anode of 0·02 mm. diameter, dissolved 317·8 μ grams at 25° with a voltage of 4·8 volts. It is shown that to get trustworthy results the deposit must not be removed from the solution and washed in the ordinary way, but must be left in position and the electrolyte displaced by water without breaking the current. Stirring of the electrolyte is essential, and in general it is shown that a micro-analysis takes as long when the electrolyte is stirred as a macro-analysis does if the electrolyte is not stirred. The treatment of the electrodes is considered at great length; it is shown that ordinary absolute alcohol is not sufficiently pure for washing the electrodes, but freshly distilled alcohol must be used for constant results. Methods are given for the estimation of mercury, copper, and silver. The cathode recommended consists of 2·70 metres of platinum wire 0·02 mm. diameter wound into a spiral. Full details of the apparatus are given in the paper, but this does not differ essentially from that used in macro-analysis except in the matter of size. The following conditions are recommended. For copper determination, an addition of 10 c.c. of 2*N* nitric acid; electrolysis at 90° with a current of 10 milliamps. at 2 volts for a period of two hours. For silver determination, an addition of 2 c.c. of 2*N* nitric acid and 1 c.c. of alcohol; electrolysis for six hours by a current of 4 milliamps. at 1·35 volts with a temperature between 50° and 60°. For mercury estimation, an addition of 2 c.c. of 2*N* nitric acid and electrolysis at 0° by a current of 10 milliamps. at 3 volts for six hours. J. F. S.

A New Method of Estimating Mercury in the Viscera. L. Tsalapatanis (*Anal. Fis. Quim., Argentina*, 1915, **3**, 84—88).—Mercury compounds present in the viscera can be estimated by

transformation into mercuric iodide, this salt being extracted with ethyl acetate and the ester evaporated. A. J. W.

New Reagent for the Detection and Colorimetric Estimation of Aluminium. F. W. Atack (*J. Soc. Chem. Ind.*, 1915, **34**, 936—937).—The author has proposed at various times the formation of a lake with alizarin as a confirmatory test for aluminium, but the reaction has failed as a direct test on account of the susceptibility of the lake to traces of acids and the interference of other metals. Alizarin-S, the sodium salt of alizarinmonosulphonic acid, however, is found to be a very sensitive reagent for aluminium.

For the detection of aluminium, 1 c.c. of a 0·1% solution of alizarin-S, which is pale yellow in the presence of acids and purple in the presence of alkalis, is added to 5 c.c. of the neutral or acid solution under examination. Ammonia is then added until the solution is alkaline, and therefore purple, when the liquid is boiled for a few moments, cooled, and acidified with dilute acetic acid. A red coloration or precipitate indicates the presence of aluminium. The compound formed seems to be the aluminium *salt* of the acid, $[C_{14}H_5O_2(OH)_2 \cdot SO_3]_3Al$, rather than a lake. The red salts of calcium, strontium, barium, zinc, and magnesium, and the salts of the other metals after group II, are soluble in acetic acid, and so do not interfere with the test. In fact, the precipitate is usually more voluminous in the presence of a calcium or zinc salt, which may be due to the formation of a lake. An example of this behaviour is described in the case of nickel. Whereas a pure nickel salt gives no coloration even with ammoniacal alizarin-S, if it contains a trace of aluminium the precipitate formed under the above conditions will contain a large amount of nickel. The test is not interfered with by phosphates or chromium, and only by comparatively large amounts of iron, but this can be overcome by the use of citric acid. The reagent will detect one part of aluminium in 10 million parts of water. All commercial samples of sodium peroxide, sodium hydroxide, hydrogen peroxide, and even the purest grades of chromium and glucinum compounds were found to contain traces of aluminium.

The test can be adapted to a colorimetric estimation of aluminium, precipitation being prevented by the addition of glycerol. The solution to be tested (5—20 c.c.) is acidified by hydrochloric or sulphuric acid, mixed with 10 c.c. of glycerol and 5 c.c. of a 1% solution of alizarin-S, then diluted to about 40 c.c., rendered slightly ammoniacal, left for five minutes, and then treated with acetic acid until the coloration is constant, and finally diluted to 50 c.c. The colour is matched against standards containing 0·005 to 0·05 mg. J. C. W.

Effect of Ammonium Chloride on Ferric and Aluminium Hydroxides During Ignition. H. W. Daudt (*J. Ind. Eng. Chem.*, 1915, **7**, 847—848).—It is unnecessary to wash precipitates of ferric and aluminium hydroxides until free from ammonium

chloride; the precipitate may, in fact, be washed with 1% ammonium chloride solution without affecting the weight of ferric oxide or alumina obtained when the precipitate is ignited. The presence of a small quantity of ammonium chloride in the wash-solution is of advantage, since it prevents the precipitate from becoming colloidal. W. P. S.

Method for Estimating Carbon-free Ash in Plant Substances. GEORGE E. BOLTZ (*J. Ind. Eng. Chem.*, 1915, **7**, 859—860).—Ash containing large quantities of calcium, magnesium, and potassium should be corrected for the amount of carbon dioxide it contains; corrections are also made for unburnt carbon and sand. From 2 to 10 grams of the material are ignited in a platinum basin until most of the carbon has been oxidised; the contents of the basin are then cooled, treated with 20 c.c. of hot water, the solution filtered into a weighed flask, and the residue washed with hot water. The filter-paper and residue are now ignited until practically all the carbon has disappeared, the ash is rinsed into the weighed flask, the contents of the latter are evaporated, the residue is dried at 110°, and weighed. The weight represents the crude ash. The flask is then connected with an apparatus for estimating carbon dioxide, hydrochloric acid being added to the flask, and the liberated carbon dioxide absorbed in 50 c.c. of 4% sodium hydroxide solution. The alkali solution is next neutralised with $N/1$ hydrochloric acid, using phenolphthalein as indicator, and then titrated with $N/20$ hydrochloric acid until neutral to methyl-orange. Each c.c. of $N/20$ hydrochloric acid used is equivalent to 0·0022 gram of carbon dioxide. Unburnt carbon, sand, and silica are estimated separately, and the sum of their weights, together with the weight of the carbon dioxide, is subtracted from the weight of the crude ash in order to obtain the amount of carbon-free ash. W. P. S.

Estimation of Methyl and Ethyl Alcohols in Spirit Varnishes. G. W. KNIGHT and C. T. LINCOLN (*J. Ind. Eng. Chem.*, 1915, **7**, 837—843).—In the absence of acetone and pyridine, the quantities of methyl and ethyl alcohols present may be estimated by the method described by Leach and Lythgoe (A., 1905, ii, 655) provided that both the sp. gr. and the refractometer number are taken into account in calculating the results. When acetone is present in the varnish, a measured quantity of the sample sufficient to yield at least 25 c.c. of distillate is distilled, air being drawn through the apparatus towards the end of the operation until no more liquid distils. The volume of the distillate is observed, and portions of it are tested for the presence of methyl alcohol and of ethyl alcohol. Should the distillate contain amyl or higher alcohols or esters, these must be removed as described by Thorpe and Holmes (T., 1903, **83**, 314). Twenty c.c. of the distillate are now added to a mixture of 20 c.c. of water and 80 grams of iodine cooled to 0°; after fifteen minutes 8 grams of red phosphorus are added and the mixture is kept at 0°, the

distillation flask containing it being attached to a reflux condenser. When violent action has ceased, the mixture is heated at 75° for twenty minutes, and then distilled into 30 c.c. of water contained in a graduated cylinder. The volume of the distillate is noted. If methyl alcohol is absent (as shown by the preliminary test), the percentage quantity of ethyl alcohol in the varnish will be $(3{\cdot}622V_1V_3)/V$, where V = volume of varnish used, V_1 = volume of the alcohol distillate, and V_3 = volume of iodides obtained. If no ethyl alcohol is present, the percentage of methyl alcohol will be $(3{\cdot}315V_1V_3)/V$, and when both alcohols are present the total quantity of alcohol is $[(0{\cdot}03315\alpha + 0{\cdot}03622\beta)V_1V_3]/V$, where α = percentage (by vol.) of methyl alcohol in the total alcohol and β = percentage of ethyl alcohol in the total alcohol. The values α and β are found from the sp. gr. of the mixed iodides. For this purpose, the latter are washed with ice-cold 1% sodium hydroxide solution, dried with potassium carbonate while kept at 0°, and the sp. gr. then determined. Then

$$\alpha = (3905 \,.\, G - G_2)/(39{\cdot}05 \,.\, G - G_2 + 51{\cdot}25 \,.\, G_1 - G),$$

where $G = D^{15{\cdot}6}_{15{\cdot}6}$ of the mixed iodides, $G_1 = 2{\cdot}292$ (sp. gr. of methyl iodide), and $G_2 = 1{\cdot}947$ (sp. gr. of ethyl iodide). If the quantity of methyl alcohol in the total alcohols is less than 10%, a modification of the Riche and Bardy method may be used for its colorimetric estimation. W. P. S.

Detection of Phytosterol in Animal Fats According to Bömer's Method by Precipitating the Phytosterol and Cholesterol with Digitonin. B. Kühn, F. Bengen, and J. Werwerinke (*Chem. Zentr.*, 1915, ii, 50—51; from *Zeitsch. Nahr. Genussm.*, 1915, **29**, 321—329).—The following procedure is recommended. The fatty acids obtained from 50 grams of the fat are warmed and treated with 25 c.c. of digitonin solution (compare A., 1914, ii, 78), the mixture is kept at 70° for one hour, 20 c.c. of chloroform are then added, the precipitate is collected on a filter, washed with chloroform and ether, and dried at 100° for ten minutes. The precipitate is then heated with 5 c.c. of acetic anhydride, the hot solution is mixed with four times its volume of 50% alcohol, cooled, the precipitate collected, washed with 50% alcohol, and recrystallised in the usual way. Animal fats usually give almost pure cholesteryl acetate after the first crystallisation, and the presence of vegetable oils is already indicated at this stage. W. P. S.

Estimation of Sugar by Allihn's Method. J. Pritzker (*Chem. Zentr.*, 1915, ii, 245: from *Zeitsch. Nahr. Genussm.*, 1915, **29**, 437—439).—To prevent discoloration of the cuprous oxide precipitate obtained in this method, the time required to dry the precipitate is shortened to less than twenty-five minutes by washing it with alcohol and ether and then suspending the filter tube vertically in the drying oven. W. P. S.

A Source of Error in the Estimation of Reducing Sugars by Collecting the Cuprous Oxide on an Asbestos Filter, Reducing it, and Weighing the Metallic Copper. H. PELLET (*Bull. Assoc. Chim. Sucr. Dist.*, 1915, **32**, 224—226).—Alkaline copper solutions extract an appreciable quantity of substance from asbestos and the latter should therefore be treated with hot sodium hydroxide solution and then washed thoroughly before it is used in filter tubes for collecting the cuprous oxide obtained in the gravimetric method of estimating reducing sugars.

W. P. S.

Preparation of a Standard Invert-sugar Solution for Use in the Estimation of Reducing Sugars by Cupropotassic Solutions. H. PELLET (*Bull. Assoc. Chim. Sucr. Dist.*, 1915, **32**, 226).—The solution is prepared by dissolving 5 grams of sucrose in 100 c.c. of water, adding 1 c.c. of hydrochloric acid, and heating the solution just to boiling, or by dissolving the same weight of sucrose in 50 c.c. of water, adding 2 c.c. of hydrochloric acid, and heating the solution at 70° for fifteen minutes. In either case, the solution is treated with 1 gram of sodium salicylate, cooled, neutralised, and diluted to 1 litre. If, during the neutralisation, a slight excess of alkali solution is introduced, the solution should be acidified immediately by the addition of a few drops of acetic acid. The invert-sugar solution thus obtained may be kept without undergoing alteration. W. P. S.

Estimation of Sucrose in Beetroots. H. COLIN (*Bull. Assoc. Chim. Sucr. Dist.*, 1915, **32**, 229—234).—Immediately after being gathered, the beetroot is treated with boiling 95% alcohol in the presence of calcium carbonate; the alcoholic solution is decanted, the beetroot is crushed in a mortar, and the extraction with alcohol continued. The united alcoholic extracts are evaporated at 35° under reduced pressure, the residue is dissolved in water, the solution treated with normal lead acetate solution, the excess of lead removed by the addition of a few drops of sodium carbonate solution, the mixture neutralised, then rendered slightly acid with acetic acid, and its volume noted (it should be about 100 c.c.). Two quantities of 50 c.c. of the solution are now placed in two flasks; to one quantity is added 5 c.c. of sucrase solution previously rendered inactive by being heated at 100°, whilst to the other is added 5 c.c. of active sucrase solution; the latter mixture is kept at 60° for one hour, then cooled, both mixtures are treated with a few drops of normal lead acetate solution, filtered, and the sugar in the filtrates estimated by polarimetric and copper-reducing methods. The author has succeeded in obtaining a very active sucrase, and will subsequently give the method of its preparation.

W. P. S.

Estimation of Starch in Cocoa by Means of Taká-diastase. CECIL REVIS and H. R. BURNETT (*Analyst*, 1915, **40**, 429—432).—Direct acid conversion of the starch in cocoa yields untrustworthy

results, owing to the presence of pentosans, etc., which yield reducing substances; better results are obtained by the use of diastase, followed by acid conversion, but here there is a distinct loss of carbohydrate during the acid conversion, whilst the use of diastase alone is attended by loss of dextrin, a portion of the latter being carried down with the precipitate formed during the subsequent clarification of the solution. When taká-diastase is used as the converter, the dextrin stage is rapidly passed and the final solution contains only maltose and dextrose, which are not affected by the clarifying agent; the quantity of these sugars is estimated by combined polarimetric and copper reduction methods. The process is as follows. Five grams of the fat-free dry cocoa are mixed thoroughly with 50 c.c. of 10% alcohol (by vol.) and the mixture is filtered under pressure; the residue is then washed with two further quantities of 50 c.c. of 10% alcohol and finally with 10 c.c. of 95% alcohol. The cocoa is now rinsed into a 250 c.c. flask with about 125 c.c. of boiling water, the flask is immersed in a boiling-water bath for fifteen minutes, the contents then cooled to 38°, 0·05 gram of taká-diastase mixed with a small quantity of water is added, followed by 2 c.c. of toluene, the flask is closed, and placed in an incubator at 38° for twenty-four hours. At the end of this time, 10 c.c. of $N/10$ sodium hydroxide solution are added, the mixture is cooled to 15°, diluted with about 100 c.c. of water, 10 c.c. of acid mercuric nitrate solution are added, and the mixture is diluted with water to 250 c.c., the volume of the toluene not being taken into account. After shaking, the mixture is filtered, 100 c.c. of the filtrate are treated with 0·5 gram of disodium hydrogen phosphate, and when this has dissolved 10 c.c. of sodium hydroxide solution are added (the strength of this alkali solution should be such that 10 c.c. nearly neutralise 4 c.c. of the acid mercuric nitrate solution; after the addition of the alkali, the mixture should have a slight acid reaction). The mixture is filtered, and 50 c.c. of the filtrate are used for the gravimetric copper estimation, polarimetric readings being also made on this filtrate. The acid mercuric nitrate solution employed is prepared by dissolving mercuric oxide in twice its weight of nitric acid (D 1·42) and diluting the solution to five times its volume with water. The following quantities of starch (calculated on the fat-free dry substance) were found in different kinds of cocoa nibs: Accra, 12·8%; Guayaquil, 8·0%; Trinidad, 14·5%; Grenada, 12·3%; San Thomé, 12·4%. Cocoa shell was found to be free from starch. W. P. S.

Application of Reactions Used in Organic Chemistry to Phytomicrochemical Investigations. C. VAN WISSELINGH (*Chem. Zentr.*, 1915, ii, 98; from *Holländische Beitr. ges. Mikrobiol.*, 1915, **3**, No. 3).—The detection of chitin is described; this substance in itself is not very sensitive towards reagents, but when heated in a closed tube at 160° with concentrated potassium hydroxide solution it is converted into chitosan. The latter is precipitated from aqueous solutions by a number of reagents, including the alkaloid

reagents, and these reactions can take place within the animal or vegetable substance containing the chitosan. If the insoluble compounds are coloured, the chitosan can be detected, after washing the substance, by means of picric acid, picrolonic acid, trinitronaphthol, trinitrocresol, and 1:2-naphthaquinone-4-sulphonic acid. Colourless, insoluble compounds may be converted into coloured substances by means of ferrocyanides and ferric salts, ferricyanides and ferrous salts, phosphomolybdic acid, and stannous chloride. The violet coloration which chitosan gives with iodine and very dilute sulphuric acid is destroyed by the addition of 66·5% sulphuric acid; if the preparation contains a cellulose membrane, this is coloured blue. All the tests can be rendered more sensitive by heating the preparation in glycerol at 300° in order to destroy interfering cell substances. W. P. S.

Gerhardt's Reaction for Acetoacetic Acid. L. Lichtwitz (*Chem. Zentr.*, 1915, i, 1343—1344; from *Berl. klin. Woch.*, 1915, **52**, 399—400).—The intensity of the coloration obtained in the ferric chloride reaction does not depend on the concentration of the acetoacetic acid, owing to the fact that acetoacetic acid has the power of changing from the ketonic form,

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2{\cdot}C_2H_5,$$

into the enolic form with the group $\cdot C(OH){:}CH{\cdot}CO$, and the latter alone gives an intense coloration with ferric chloride. In the case of urine containing acetoacetic acid there is probably a mixture of both forms. Investigation has shown that the enolic form is present when the acetoacetic acid content exceeds 0·05%. At the commencement of acidosis the urine contains only the ketonic form, the enolic form appearing as the concentration of the latter increases. A positive reaction with ferric chloride indicates, therefore, serious derangement. W. P. S.

Detection of Citric Acid in Wine. E. Baier and P. W. Neumann (*Chem. Zentr.*, 1915, ii, 205—206; from *Zeitsch. Nahr. Genussm.*, 1915, **29**, 410—411).—Twenty-five c.c. of the wine are neutralised, then rendered acid with acetic acid, 3 grams of blood-charcoal free from calcium carbonate are added, the mixture is shaken for ten minutes, and filtered. Ten c.c. of the filtrate are treated with 1 c.c. of Denigès's reagent (5 grams of mercuric oxide dissolved in a mixture of 20 c.c. of concentrated sulphuric acid and 100 c.c. of water), boiled, filtered if a precipitate forms, 1% potassium permanganate solution is then added drop by drop until manganese dioxide begins to separate, and the latter is dissolved by the addition of hydrogen peroxide. If citric acid is present, the mixture at this stage exhibits a white turbidity or a precipitate may form. The precipitate (the mercury salt of acetonedicarboxylic acid) is then collected on a small filter, washed three times with cold water, dissolved in 3 c.c. of 10% sodium chloride solution, and a few drops of dilute ferric chloride solution are added. A raspberry-red coloration is obtained if the wine contained citric acid. W. P. S.

Detection and Estimation of Benzoic Acid in Animal Foods. K. BAUMANN and J. GROSSFIELD (*Chem. Zentr.*, 1915, ii, 202—203; from *Zeitsch. Nahr. Genussm.*, 1915, **29**, 397—409).—The authors have investigated several methods which have been described for the detection of benzoic acid in foods, particularly those proposed by Mohler (compare Halphen, A., 1908, ii, 906), Jonescu (A., 1909, ii, 627), and von der Heide and Jakob (A., 1910, ii, 359); preference is given to Mohler's method, a reaction being obtained with 0·1 mg. of benzoic acid. In certain cases, Jonescu's test fails to detect the presence of a relatively large quantity (some mg.) of the acid. The following method is given for the estimation of benzoic acid; it consists in converting the benzoic acid into its alkali salt, precipitating soaps by the addition of calcium chloride and proteins by phosphotungstic acid, and extracting the benzoic acid with carbon tetrachloride. *In milk:* One hundred c.c. of the milk are treated with phenolphthalein solution, and concentrated potassium carbonate solution is added until a permanent red coloration is obtained; the mixture is then diluted to 200 c.c., 20 c.c. of 20% calcium chloride solution are added, the whole is heated for fifteen minutes on a water-bath, cooled, and diluted to 250 c.c. The mixture is now filtered (old milks sometimes yield a turbid filtrate, but this does not affect the process), 175 c.c. of the filtrate are transferred to a 200 c.c. flask, a few drops of copper sulphate solution and 10 c.c. of sodium phosphotungstate solution (200 grams of sodium tungstate and 120 grams of sodium phosphate per litre) are added, and the contents of the flask are diluted with sulphuric acid (1 : 3) to 200 c.c. After eighteen hours the mixture is filtered, 100 c.c. of the filtrate are percolated for six hours with carbon tetrachloride, the latter is separated, mixed with an equal volume of neutral alcohol containing phenolphthalein, and the solution is titrated with $N/10$ alkali hydroxide solution. Milk free from benzoic acid yields a carbon tetrachloride extract which requires 0·1 c.c. of $N/10$ alkali solution for neutralisation; allowing for this correction, the quantity of benzoic acid present in a sample is found from the equation $x=0{\cdot}03486(n-0{\cdot}1)$ gram, where $n=$c.c. of $N/10$ alkali solution used. *In fats, etc.:* Fifty grams of the fat, such as butter or margarine, are melted in a beaker, dissolved in benzene, the solution is washed with ether into a separating funnel (any insoluble portion may be left in the beaker), and shaken with 20 c.c. of warm potassium carbonate solution; if the red coloration disappears, more of the potassium carbonate solution must be added. The aqueous layer is then drawn off into the beaker, and the fatty layer is extracted several times with hot water. The united aqueous extracts are then treated with 20 c.c. of calcium chloride solution, a few pieces of pumice-stone are added, and the solution is evaporated in a basin until all odour of benzene has disappeared. The solution is now transferred to a 200 c.c. flask, and the process continued as described under milk. The quantity of benzoic acid present is calculated from the equation $x=27{\cdot}88(n-p)$ mg., where p is the number of c.c. of $N/10$ alkali solution used by 100 grams of different fats free from

benzoic acid. For lard the correction is 0·05 c.c., for butter 0·50 c.c., and for palm oil 0·30 c.c. W. P. S.

Apparatus for Fat Extraction. I. SELECTER (*J. Ind. Eng. Chem.*, 1915, **7**, 871—872).—The apparatus consists of three simple parts connected one above the other by ground-in joints. The upper part consists of a cylindrical tube constricted near its lower end; a tubular condenser fits into the top of this cylinder and an extraction tube carrying a siphon in the lower end. The middle part of the apparatus comprises a cylindrical tube holding the extraction thimble containing the substance, and the lower end of this tube is connected with the flask in which the solvent is placed. The condensed liquid falling from the condenser collects in the siphon tube, is discharged periodically from the latter into the extraction thimble, and then passes directly into the flask. During the intervals of the action of the siphon, the substance in the thimble is heated by the ascending vapours of the solvent.

W. P. S.

Rapid Method for the Estimation of Water and Fat in Butter and Margarine. A. A. BESSON (*Chem. Zeit.*, 1915, **39**, 770—772).—The apparatus used in the estimation of the water consists of two aluminium basins placed one within the other; the outer basin has a diameter of 8 cm., whilst that of the inner basin is 6 cm. Both basins have vertical walls, the outer one being 2·5 cm. high, the inner 1·5 cm. A wire arrangement over the inner basin supports an inverted aluminium funnel, the lower edge of which is below the top of the wall of the outer basin. A weighed quantity (5 grams) of the butter or margarine is placed in the inner basin, the whole apparatus is weighed, placed in an oven at 160° for twenty minutes, cooled, and again weighed, the loss in weight giving the amount of water present. The fat is estimated by mixing 5 grams of the sample with 40 c.c. of hydrochloric acid (2 : 1) in a beaker, heating the mixture for one minute on an asbestos plate, and then transferring it to an instrument termed a "sapometer," adding 100 c.c. of ether and a quantity of water sufficient to bring the ethereal layer into the graduated part of the apparatus, shaking the mixture, and, when the ethereal layer has separated, noting its volume; an aliquot portion is then drawn off into a weighed flask, the solvent evaporated, the residue of fat dried, and weighed. W. P. S.

Detection of Acetone by Frommer's Test. N. O. ENGFELDT (*Chem. Zentr.*, 1915, ii, 100; from *Berl. klin. Woch.*, 1915, **52**, 458—459).—Fromer's test depends on the fact that acetone condenses with salicylaldehyde in the presence of alkali hydroxide to form a red substance, di-*o*-hydroxydistyryl ketone. Ten c.c. of the urine are treated with 1 gram of solid potassium hydroxide, and, without waiting for the alkali to dissolve, ten drops of 10% salicylaldehyde solution (in alcohol) are added and the mixture is heated to 70°. If acetone is present, a purple-red

zone appears at the junction of the two liquids. The test will detect 0·05 mg. of acetone in 10 c.c. of water, but the author finds that it may be rendered more sensitive and capable of detecting 0·001 mg. of acetone in 10 c.c. when modified as follows. Ten c.c. of the distillate from the urine are mixed with 5 grams of solid potassium hydroxide and five drops of concentrated salicylaldehyde solution, the test-tube containing the mixture is placed in a water-bath at 50°, and the water is heated gradually to boiling. As the potassium hydroxide dissolves a crystalline mass is formed which, in the presence of acetone, is coloured bright red. Formaldehyde, acetaldehyde, formic acid, lactic acid, phenols, and alcohol do not give the red coloration, but acetoacetic acid and β-hydroxybutyric acid yield red-coloured compounds with the test. On account of its sensitiveness, the test is not suitable for clinical purposes.

W. P. S.

Extraction of Caoutchouc, etc., with Acetone. A. Hutin (*Ann. Chim. anal.*, 1915, **20**, 212—213).—The residue obtained on evaporating the acetone extract of caoutchouc, etc., should be dried under reduced pressure. If the residue is dried in an ordinary steam-oven, it increases in weight, and this increase may amount to 20%, or more, of the actual weight of the residue. W. P. S.

New Rapid and Exact Method of Estimating Alkaloids in Cinchona Bark. Francesco Lenci (*Boll. chim. farm.*, 1915, **54**, 417—422).—As a method of estimating the alkaloids in cinchona bark, Hager (*Zeitsch. anal. Chem.*, 1869, **8**, 477; 1882, **21**, 415) suggested the precipitation of the alkaloids as picrates and the weighing of the precipitate on a tared filter after drying at 40°. This precipitation is accompanied by coagulation of the proteins, waxy matter, etc., high results being consequently obtained. The author finds that the following procedure gives good results.

To 5 c.c. of a solution of the hydrogen sulphate of the alkaloid are added 50 c.c. of a cold, saturated picric acid solution, the titre of which has been determined by the "nitron" method (compare Busch and Blume, A., 1908, ii, 328). After half an hour the liquid is filtered, and the residual picric acid in 5 c.c. of the filtrate estimated by precipitation with nitron. Multiplication of the amount of picric acid thus formed by eleven, and subtraction of the product from the picric acid content of the 50 c.c. of precipitant, gives the quantity of the acid which has combined with the amount of alkaloid taken. The results obtained in this way with solutions of various concentrations of the acid sulphates of quinine, cinchonine, cinchonidine, and quinidine show that, in all cases, 2 mols. of picric acid combine with 1 mol. of the alkaloid. These results were controlled by, and found to agree with, estimations of the picric acid in the alkaloid precipitates, the latter being heated with dilute sulphuric acid and the liberated picric acid precipitated by means of nitron.

For the various alkaloids, the factors by which the amounts of picric acid in the precipitates must be multiplied in order to arrive

at the corresponding quantities of alkaloid are: for quinine and quinidine, 0·7075; and for cinchonine and cinchonidine, 0·6419. For the complex mixture of alkaloids in cinchona bark, the mean factor, 0·6738, gives approximately exact results.

The method given in the Italian "Farmacopea Ufficiale" for estimating the alkaloids in cinchona bark consists in weighing the residue of the chloroform extract after distillation of the solvent. The author finds that this method gives results which, on the average, are 1·2% in excess of the true values. T. H. P.

Improvements in the Method of Analysis of Proteins by Determination of the Chemical Groups Characteristic of the Different Amino-acids. Donald D. Van Slyke (*J. Biol. Chem.*, 1915, **22**, 281—285).—Modifications are described in the author's method which improve it. The main points refer to the washing of the phosphotungstic precipitate, and the decomposition of the basic phosphotungstate; for the latter purpose, instead of the barium method, repeated extraction with equal parts of ether and amyl alcohol is now recommended; this completely removes phosphotungstic acid. W. D. H.

Method for the Estimation of the Tryptophan-content of Proteins involving the Use of Baryta as a Hydrolysing Agent. Annie Homer (*J. Biol. Chem.*, 1915, **22**, 369—389).—The hydrolysis of proteins by baryta, and the precipitation of the tryptophan from the mixture with mercury sulphate, followed by bromination, is advocated for its ease and accuracy. Cystine is not destroyed, neither is there any loss of tryptophan. There is also no appreciable formation of derivatives which affect the final estimation with bromine. W. D. H.

The Use of Aluminium Hydroxide Cream for the Removal of Albumin in Nitrogen Partition in Urinary Analysis. Grover Tracy and Willam H. Welker (*J. Biol. Chem.*, 1915, **22**, 55—57).—The cream does not remove any nitrogen from normal urine, but can be used for the removal of albumin without affecting the normal nitrogenous constituents. W. D. H.

A Micro-refractometric Method of Estimating Globulin and Albumin in Small Quantities of Serum. T. Brailsford Robertson (*J. Biol. Chem.*, 1915, **22**, 233—239).—The method is similar on a reduced scale to that already described. Four quantities are determined, albumin, globulin, total protein, and non-proteins. From 0·5 to 1·5 c.c. of serum is enough. W. D. H.

Picric Acid and Malingering. Et. Barral (*J. Pharm. Chim.*, 1915, [vii], **12**, 228—229; from *Soc. Biol.*, 1915, 453).—Doses of 0·3 gram of picric acid taken twice weekly cause the urine to be coloured red; that this coloration is not due to the presence of blood in the urine may be shown by the detection of picramic acid in the latter. The following tests may be applied for this purpose: (1) the colour of the urine changes to yellow on the addition of an acid; (2) the urine, when treated with basic lead acetate solution, yields a flesh- or salmon-coloured precipitate; (3) barium

chloride gives a characteristic light orange precipitate; (4) zinc sulphate gives a yellowish-brown, more or less orange-coloured precipitate; (5) when the urine is extracted with ethyl acetate the yellow-coloured extract dyes wool red. W. P. S.

The Estimation of the Bile Salts in Urine by Means of the Surface Tension Method. GEORGE DELWIN ALLEN (*J. Biol. Chem.*, 1915, **22**, 505—524).—If peptonuria and acetonuria are absent, and the urine is diluted to D 1·010, the main error in the estimation of bile salts by the surface tension method is due to varying acidity. The data presented allow, however, of the construction of a table showing the amounts of sodium glycocholate which should be present in urines of observed surface tension. This is not quite analogous to bile salts actually excreted by the kidney, for taurocholate is present too, and this salt lowers the tension less than the glycocholate. Bile pigment has no effect. Stalagmometric measurements, although disappointing so far as regards absolute accuracy, are believed to prove clinically valuable. W. D. H.

Studies of the Culture Media Employed for the Bacteriological Examination of Water. III. Composition of the Gases Formed in Lactose-Peptone Fermentation Tubes. E. M. CHAMOT, C. M. SHERWOOD, and R. C. LOWARY (*J. Amer. Chem. Soc.*, 1915, **37**, 2198—2204).—In an earlier paper (this vol., ii, 712) it has been shown that the volumes of the gases formed by fæcal bacteria in lactose-peptone media are proportional to the concentration of the peptone. With regard to the composition of the gases, it has been found that with increase of peptone the percentage of carbon dioxide increases and that of hydrogen decreases until in each case an equivalent of approximately 4% of peptone is reached, after which the percentages of these gases remain practically constant. The "gas-ratio" varies with the concentration of the nitrogenous material present in the medium. Methane is not found unless the inoculated medium is exposed to the air for more than twenty-four hours. About 2—3% of nitrogen is found in the gases. The gases formed in a medium containing 1% of peptone were: carbon dioxide, 26·9%; hydrogen, 70·2%; nitrogen, 2·9%. In a medium containing 4% of peptone the composition of the gases was: carbon dioxide, 38·0%; hydrogen, 58·3%; nitrogen, 2·7%. An excess of oxygen retards the formation of gas, and tends to increase the percentage of carbon dioxide. E. G.

Effect of Grinding the Soil on its Reaction as Determined by the Veitch Method. P. E. BROWN and H. W. JOHNSON (*J. Ind. Eng. Chem.*, 1915, **7**, 776—777).—Soils should not be ground previous to testing their reactions by the Veitch method. When acid soils are ground, the acidity is reduced, and the reaction frequently becomes basic. The basicity increases with the grinding of the soil, the increase depending on the amount of sand present; it is greater in coarse, sandy soils than in fine sands.

W. P. S.

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ii, 911	ii.	18	*for* "**Hartley**, *Harold Brewer*," read "**Hartley**, *Harold.*"

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i, 193	6	,,	"some" *read* "sour."
i, 193	8*	,,	"360" *read* "361."
i, 346	13*	,,	"BATELLI" *read* "BATTELLI."
i, 472	3*	,,	"BRONNENFENNER" *read* "BRONFENBRENNER."
i, 520	11*	,,	"dibromo-" *read* "tribromo-."
i, 525	18	,,	"Magnesium ethyl iodide" *read* "magnesium methyl iodide."
i, 562	9, 11	,,	"α-bromo*iso*butyl" *read* "α-bromo*iso*butyryl."
i, 634	2	,,	"Griebold" *read* "Griebel's."
i, 646	18, 21, 3*	,,	"gynocardinic" *read* "gynocardic."
	22*, 8*	,,	"*gynocardinate*" read "*gynocardate.*"
	5*	,,	"hydroxygynocardinic" *read* "hydroxygynocardic."
i, 674	15*	*after*	"1267" *insert* "; from *Öster. Chem. Zeit.*, 1914, **17**, 323—333."
i, 692	21*	,,	"473" *insert* "; from *Philippine J. Sci.*, 1913, [A], **8**, 399—426."
i, 708	2*	,,	"1456" *insert* "; from *Sitzungsber. Heidelberg. Akad. Wiss. Math. Naturw. Klasse.*, [A], 1914, 18."
i, 714	19*	,,	"1165" *insert* "; from *Sitzungsber. Math. Naturwiss. Klasse, K. Akad. Wiss. Wien*, 1914, reprint."
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ii, 251	7*	*for*	"HENDEN" *read* "HINDEN."
ii, 258	20	,,	"maximum" *read* "minimum."
ii, 280	5	,,	"not denied" *read* "denied."
ii, 357	14	,,	"Wurtzite" *read* "Hauerite."
ii, 357	21	,,	"V. J. VERNADSKI" *read* "V. I. VERNADSKI."
ii, 357	29	,,	"**Grahnite**" *read* "**Gahnite.**"
ii, 452	8*	,,	"Biol. Zentr." *read* "Bied. Zentr."

* From bottom.

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ii,	574	15*	,, "MISSON SERAING" *read* "MISSON."
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ii,	651	14*	,, "sodium" *read* "hydrogen."
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ii,	758	8*	*for* "molecular" *read* "unimolecular."
ii,	828	4	,, "VII" *read* "III."

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